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(54) Title: LONG CHAIN BRANCHED ETHYLENE HOMOPOLYMER MADE BY A SLURRY PROCESS AND BLENDS THEREOF		
(57) Abstract The present invention relates to a novel ethylene polymer having long chain branches and made by a continuous slurry polymerization process. In general, the slurry polymerization process comprises a supported catalyst and ethylene conversion rates greater than 92 percent. More particularly, the present invention is concerned with a novel ethylene polymer having unique molecular and comonomer features as well as long chain branching wherein the polymer is made by a continuous slurry loop polymerization process in the presence of a solid supported constrained geometry catalyst system. The unique features pertain to a novel ethylene homopolymer characterized as having a high density and a M_w/M_n ratio which decreases as molecular weight increases and a novel ethylene interpolymer characterized as having a reversed comonomer distribution relative to conventional Ziegler-catalyzed ethylene interpolymers. The invention also relates to blend compositions containing the novel ethylene polymer obtained by dry or melt mixing the already produced components, or through <i>in situ</i> production by in parallel or in series arranged reactors. The novel ethylene polymers can be used in applications such as films, blow molded, injection molded, and rotomolded articles, fibres, coating, and cable and wire coatings and jacketings and various forms of pipe.		

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LONG CHAIN BRANCHED ETHYLENE HOMOPOLYMER MADE BY A SLURRY PROCESS AND BLENDS THEREOF

The present invention relates to a novel ethylene polymer having
5 long chain branches and made by a continuous slurry polymerization
process. In general, the slurry polymerization process comprises a
supported catalyst and ethylene conversion rates greater than 92 percent.
More particularly, the present invention is concerned with a novel
ethylene polymer having unique molecular and comonomer features as well as
10 long chain branching wherein the polymer is made by a continuous slurry
loop polymerization process in the presence of a solid supported
constrained geometry catalyst system. The unique features pertain to a
novel ethylene homopolymer characterized as having a high density and a
 M_w/M_n ratio which increases as molecular weight increases and a novel
15 ethylene interpolymer characterized as having a reversed comonomer
distribution relative to conventional Ziegler-catalyzed ethylene
interpolymers.

Polymerization of ethylene using coordination catalysts can be
carried out in the high pressure, solution, slurry (suspension) or gas
20 phase polymerization processes. The slurry and gas phase processes are
examples of the so called particle form process. In a slurry
polymerization process, the catalyst is typically supported on an inert
carrier. The polymerization is then carried out at temperatures below the
melting point of the polymer, thereby precipitating the polymer onto the
25 carrier. This results in the polymer powder particles growing while being
suspended in a diluent (slurry). The relatively low polymerization
temperatures which are characteristic of most slurry processes permits the
manufacturing of polymers of very high molecular weight. However, in
general, relatively low polymerization reaction temperatures result in low
30 ethylene conversions rates.

Various vessels can be used to polymerize ethylene. Suitable
vessels or reactors include autoclaves (that is stirred tank reactors),
tubes, loops, spheres and combinations thereof in multiple reactor
configurations. Slurry loop reactors are used commercially by
35 manufacturers such as Phillips, BASF and Chevron. Journal of Applied
Polymer Science: Applied Polymer Symposium, 36 49-60 (1981) describes the
conventional Phillips loop reactor process, including diluents and

catalyst systems, for polymerizing ethylene. In U.S. Patent No. 5,705,578, Phillips describes a slurry polymerization using a metallocene catalyst system and a continuous loop reactor with isobutane. EP 479 186A2 describes a loop reactor system for producing ethylene polymers.

5 But known slurry processes are not known or described to provide ethylene polymers characterized as having long chain branching.

Further, WO 97/368442 describes ethylene solution polymerization in the presence of constrained geometry catalyst systems in a loop reaction system having a high volumetric heat removal rate.

10 For slurry polymerizations, supported versions of constrained geometry catalysts have developed such as those disclosed in WO 96/16092 and WO 96/28480. In these systems, the active form of the catalyst is strongly associated with the support and thus does not diffuse into the diluent at typical slurry polymerization process conditions. As described

15 in U.S. application numbers 08/857,816 and 08/857,817, the ethylene polymers that result from slurry polymerizations using supported constrained geometry catalyst systems are characterized as having unique molecular and compositional features. U.S. application number 08/857,817 (Attorney Docket No. 41886B) describes ethylene homopolymers and blends

20 therewith wherein the homopolymers are characterized having a high density as well as a narrow M_w/M_n at high molecular weight and a broader M_w/M_n at low molecular weight (that is, a M_w/M_n which decreases when molecular weight increases). U.S. application number 08/857,816 (Attorney Docket No. 41886C) describes ethylene copolymers and blends therewith wherein the

25 copolymers are characterized as having a reversed comonomer distribution relative to conventional Ziegler-catalyzed ethylene/ α -olefin copolymers.

Given the unique molecular and comonomer features of ethylene polymers manufactured using a slurry polymerization process and supported constrained geometry catalyst systems, several important performance

30 improvements result. For example, the polymers contain few impurities such as wax, gels and the like and, as such, wax buildup on die lips, smoke generation during extrusion and off taste and odor problems in fabricated articles are all minimized. Additionally, the polymers are described as having high impact strength and excellent (environmental

35 stress crack resistance) ESCR.

Although exhibiting many performance improvements relative to conventional Ziegler-catalyzed polymers and ordinary single-site catalyst systems, known ethylene/ α -olefin polymers manufactured using a slurry polymerization process and constrained geometry catalyst systems (or any
5 other single-site catalyst system, supported or unsupported), have not been characterized as having improved processability. That is, these polymer have not been described as providing lower amperage and die back pressure during extrusion or improved resistance to the onset of melt fracture).

10 A known solution for providing improved processability is to manufacture ethylene polymer having long chain branching as taught by Lai et al. in U.S. Patent Nos. 5,272,236, 5,278,272 and 5,665,800. While Lai et al. exemplify the use of unsupported constrained geometry catalysts in a continuous solution polymerization process which consisted of autoclaves
15 or stirred tank reactors to manufacture ethylene homopolymers and ethylene/ α -olefin interpolymers having long chain branching, the Examples reported in U.S. application numbers 08/857,816 and 08/857,817 were manufactured using a supported constrained geometry catalyst in a continuous slurry polymerization process consisting of autoclave or
20 stirred tank reactors. The resulting polymers described in U.S. application numbers 08/857,816 and 08/857,817 are not described as having long chain branching (that is, containing more than 0.01 long chain branch per 1000 carbons atoms), nor are they described as having improved resistance to the onset of melt fracture in gas extrusion rheology tests.

25 Therefore, there is need for a process of making ethylene polymers having unique molecular or comonomer features (that is, ethylene homopolymers characterized as having a high density and a M_w/M_n ratio which decreases as molecular weight increases and ethylene interpolymers characterized as having a reversed comonomer distribution) as well as
30 containing long chain branching (which may be manifested by an improved resistance to the onset of melt fracture).

The broad aspect of the invention is an ethylene polymer characterized as having long chain branches and manufactured by a continuous high conversion rate slurry polymerization reaction process in
35 the presence of a supported constrained geometry catalyst system. The process comprises polymerization of at least ethylene in the presence of a

solid supported catalyst system,

the catalyst system comprising a support or carrier material,
a transition metal compound, and an activator capable of converting the
transition metal compound into a catalytically active transition metal
5 complex,

wherein:

- (i) the active species of the catalyst is strongly associated with a carrier, such that the species is not liberated from the carrier and does not escape from the polymer being produced;
- 10 (ii) the transition metal of the transition metal compound is selected from Group 3 to 5 of the Periodic Table;
- (iii) the polymerization reaction is conducted by slurry polymerization so that solid polymer particles are produced and maintains the solid state during the reaction; and
- 15 (iv) the polymerization reaction is conducted at ethylene conversion rates of greater than 92 percent, preferably greater than or equal to 95 percent, more preferably greater than or equal to 98 percent, per pass and preferably at reaction temperatures greater than 50°C, especially greater than or equal to 60°C, more especially greater than or
20 equal to 70°C, most especially in the range of from 70°C to 110°C using a hydrocarbon diluent, preferably a branched paraffin (for example, isopentane, isobutane, dimethylpropane, dimethylenebutane or dimethylpentane), more preferably isobutane or dimethylpropane, most preferably isobutane, that mitigates against agglomeration at such rates
25 and temperatures.

In another embodiment, the invention pertains to a slurry loop polymerization process. In this embodiment, an ethylene homopolymer or interpolymer is manufactured in a slurry polymerization process for polymerizing ethylene in at least one slurry reaction stream of at least
30 one reactor with a supported solid catalyst system and diluent, the process comprising an ethylene conversion rate of greater than or equal to 92 percent per pass and:

- (a) at least one flow loop which forms the at least one

reactor, the at least one flow loop having:

- (1) at least one product outlet,
- (2) at least one catalyst inlet through which catalyst continuously flows into the at least one flow loop,
- 5 (3) at least one monomer inlet through which monomer continuously flows into the at least one flow loop and, with catalyst and diluent, forms the at least one slurry reaction stream,
- (4) at least one heat exchange apparatus which continuously receives the slurry reaction stream and polymer formed therein, and which continuously removes heat of reaction or
10 polymerization from the at least one flow loop, and
- (5) at least one pump apparatus for continuously pumping the slurry reaction stream and polymer around the at least one flow loop, and

- 15 (b) a portion of the slurry reaction stream and the ethylene homopolymer or interpolymer continuously exiting the at least one flow loop through the at least one product outlet,

wherein the ethylene homopolymer is characterized as having long chain branching and:

- 20 (i) a M_w/M_n ratio greater than 2.5 which satisfies the following inequality:

$$M_w/M_n \geq 22.8 - 3.3 \log M_n$$

- (ii) a melt index (I_2) of from 0.0001 to 10000 g/10 min., and

25

- (iii) a density satisfying the following inequality:

$$\text{density (g/cm}^3\text{)} > 0.9611 + 0.0058 \log (I_2) - 0.00128 \log^2 (I_2),$$

and

- wherein the ethylene interpolymer comprises ethylene interpolymerized
30 with at least one comonomer selected from the group consisting of a compound represented by the formula $H_2C = CHR$ wherein R is a C_1 - C_{20} linear, branched or cyclic alkyl group or a C_6 - C_{20} aryl group, and a C_4 -

C₂₀ linear, branched or cyclic diene and is characterized as having long chain branching and the following combination of properties:

(iv) a density of from 0.87 to 0.98 g/cm³;

5 (v) M_w/M_n of from 2.5 to 10, wherein M_w and M_n are, respectively, a weight average molecular weight and a number average molecular weight, both as measured by gel permeation chromatography (GPC);

(vi) a slope of cross-fractionation (SCF), as determined using cross-fractionation chromatography (CFC), in the range of
10 from - 1 to - 0.005; and

(vii) a sum of extractives at reduced temperature, as determined using cross-fractionation chromatography (CFC), of less than or equal to 8 percent by weight, based on the total amount of fractions extracted at temperatures in the overall range of
15 extraction temperatures in CFC, excluding purge.

In another aspect, the present invention also provides an ethylene polymer prepared by a process, the process comprising polymerizing ethylene under slurry process conditions in a loop reaction system with a supported catalyst system, the catalyst system comprising:

20 (I) a supported catalyst component resulting from admixing:

(a) a support material;

(b) an organometal compound which is a member of Groups 2-13 of the Periodic Table of the Elements, germanium, tin, or lead;

25 (c) an activator compound containing a cation which is capable of reacting with a transition metal compound to form a catalytically active transition metal complex, and a compatible anion having up to 100 nonhydrogen atoms and containing at least one substituent comprising an active hydrogen moiety; and

30 (d) a transition metal compound; or

(II) a supported catalyst component resulting from admixing

(a) a support material and an alumoxane which component contains 15 to 40 weight percent of aluminum, based

on the total weight of the support material and alumoxane, which is obtained by;

(i) heating said support material and alumoxane under an inert atmosphere for a period and at a temperature sufficient to fix alumoxane to the support material, to provide a supported catalyst component wherein not more than 10 percent aluminum present in the supported catalyst component is extractable in a one-hour extraction with toluene at 90°C using 10 ml toluene per gram of supported catalyst component; and

(ii) optionally, subjecting the product produced in step (i) to one or more wash steps to remove alumoxane not fixed to the support material; and

(b) a transition metal compound; or

(III) any combination of I and II.

In another aspect, the present invention also provides a polymer blend composition comprising:

(A) the ethylene polymer described herein above in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B) and

(B) an ethylene polymer other than one having the identical properties of Component A in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B).

Another embodiment of the invention is a process for forming a polymer blend composition, the process comprising the steps of:

(I) preparing the ethylene polymer (A) described above;

(II) contacting under polymerization conditions a reaction stream comprising ethylene, optionally at least one α -olefin comonomer, and an ethylene polymerization catalyst, to form (B) an ethylene polymer other than one having the identical properties of Component (A); and

(III) combining the ethylene polymer (A) with the ethylene polymer (B) to form (C) the polymer blend composition.

Another aspect of the invention is a slurry polymerization process

for polymerizing ethylene in a slurry reaction stream of two or more reactors with at least one supported solid catalyst system and diluent, the process comprising an ethylene conversion rate of greater than or equal to 92 percent per pass and:

5 (a) a first flow loop which forms a first reactor, the first flow loop having:

- (i) at least one first product outlet,
- (ii) at least one first catalyst inlet through which
10 the at least one supported solid catalyst system continuously flows into the first flow loop,
- (iii) at least one first monomer inlet through which monomer continuously flows into the first flow loop and, with the catalyst system and diluent, forms a first slurry reaction stream,
- (iv) at least one first heat exchange apparatus which
15 continuously receives the first slurry reaction stream and first polymer formed therein, and which continuously removes heat of reaction or polymerization from the first flow loop, and
- (v) at least one first pump apparatus for
20 continuously pumping the first reaction stream and first polymer in the first flow loop from the at least one first heat exchange apparatus to the at least one first product outlet, and

(b) a second flow loop which forms a second reactor, the second flow loop having:

- (i) at least one second product outlet,
- (ii) optionally, at least one second catalyst inlet
25 through which catalyst continuously flows into the second flow loop,
- (iii) at least one second monomer inlet through which monomer continuously flows into the second flow loop and, with catalyst and solvent or diluent, forms a second reaction stream,
- (iv) at least one second heat exchange apparatus
30 which continuously receives the second reaction stream and second

polymer formed therein, and which continuously removes heat of reaction or polymerization from the second flow loop, and

(v) at least one second pump apparatus for continuously pumping the second reaction stream and second polymer in the second flow loop from the at least one second heat exchange apparatus to the second product outlet, and

(b) the second flow loop having at least one product inlet into which continuously flows the first polymer and a portion of the first reactor stream from the at least one first product outlet of the first flow loop, and

(c) a portion of first polymer, second polymer, first reaction stream and second reaction stream continuously exiting the second flow loop through the at least one second product outlet.

The surprising and unique feature of the present invention is by operating a slurry polymerization process continuously at high conversion rates in the present of a supported constrained geometry catalyst system, ethylene homopolymers and interpolymers having unique molecular or comonomer features and long chain branching can be manufactured.

The properties of the ethylene homopolymer of the present invention are important for applications where a high density is needed to ensure certain mechanical properties such as, for example, abrasion resistance, indentation resistance, pressure resistance, topload resistance, modulus of elasticity, or morphology (for the chlorination of PE to CPE).

In addition to improved melt or extrusion processability, the long chain branching provides several important advantages such as, for example, improved heat shrink, improved irradiation efficiency, improved resistance to draw resonance.

Advantages of using the novel ethylene homopolymer in blend compositions is that, for a given molecular weight, its increased density over conventional ethylene homopolymers permits the incorporation of more comonomer in the second component of the blend. This, in turn, results in increased tie molecule formation and improvement in properties such as ESCR, toughness and impact strength. The blend can be obtained by dry or melt mixing the already produced components, or through in-reactor

production using multiple reactors which can be autoclave or loop reactors in either parallel and/or series configurations.

5 The inventive ethylene interpolymer contains substantially no impurities such as a wax, a gel and the like, and possesses a comonomer content distribution in which the lower the molecular weight of an interpolymer fraction, the lower the comonomer content and, conversely, the higher the molecular weight of an interpolymer fraction, the higher the comonomer content.

10 The ethylene homopolymer and interpolymer of the present invention can be used in applications where improved impact resistance, improved modulus of elasticity, high slow and rapid crack propagation resistance, improved ball indentation hardness and improved notched impact strength are desired. Such applications include, but are not limited to, sintering powders (for example, where ultra high molecular weight polyethylene
15 powder is incorporated as a fused component of surfaces which are required to have high abrasion resistance including gear wheels of machinery, the lower surfaces of ski's, chlorinated polyethylene (CPE) feedstock resins, films, blow molded, injection molded, and rotomolded articles, fibres, and cable and wire coatings and jacketings and, various pipe applications.

20 These and other features of the present invention will become apparent with reference to the following descriptions and appended claims.

FIG. 1 is a contour plot of extraction temperature, molecular weight and molecular weight distribution, as determinable using cross-fractionation chromatography.

25 FIG. 2 is an integral curve of the amount extracted relative to extraction temperature, as determinable using cross-fractionation chromatography.

FIG. 3 is a plot of molecular weight and comonomer content distribution, as determinable using gel permeation chromatography/Fourier
30 transformation infrared spectroscopy (GPC/FT-IR).

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the Group or

Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32, etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The term "hydrocarbyl" as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or aliphatic substituted cycloaliphatic groups.

The term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "silyl" means a group having a silicon linkage between it and the carbon atom to which it is attached.

The term "germyl" means a group having a germanium linkage between it and the carbon atom to which it is attached.

The term "Bronsted Acid cation" means a cation which acts as a proton donor.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer. Thus the term "interpolymer" embraces and includes copolymers and terpolymers.

By the term "reversed comonomer distribution" it is meant that the lower the molecular weight of an interpolymer fraction, the lower the comonomer content of that fraction and, conversely, the higher the molecular weight of an interpolymer fraction, the higher the comonomer content of that fraction. Thus, the comonomer distribution is not uniform in the sense of the polymer having a narrow short chain branching distribution as determined using temperature rising elution fractionation techniques. Nor does the comonomer distribution follow that of conventional Ziegler heterogeneous ethylene polymers wherein the lower the molecular weight of an interpolymer fraction, the higher the comonomer content of the fraction; and the higher the molecular weight of the interpolymer fraction, the lower the comonomer content of the fraction.

The density of the ethylene polymer compositions of the present invention is measured in accordance with ASTM D-792. The molecular weight of the ethylene polymer compositions of the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as I_2). Also, melt index determinations can be made using other conditions such as at 190°C/5 kg, 190°C/10 kg and 190°C/21.6 kg. Such determinations are known as I_5 , I_{10} , and I_{21} respectively.

Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. Other useful physical property determinations made on the novel polymer compositions described herein include the melt flow ratio (MFR): measured by determining " I_{10} " (according to ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition (N)") and dividing the obtained I_{10} by the I_2 . The ratio of these two melt index terms is a melt flow ratio which is designated as I_{10}/I_2 . Other melt flow ratio determinations include $I_{21.6}/I_5$ and $I_{21.6}/I_2$.

Except in respect of cross-fractionation chromatography (CFC) and comonomer distribution, the molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the ethylene polymers and the various blends of the present invention can be conveniently determined by gel permeation chromatography (GPC) using a Waters 150C high temperature chromatographic unit equipped with a differential refractometer and three columns of mixed

porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of 10^3 , 10^4 , 10^5 and 10^6\AA . The solvent is 1,2,4-trichlorobenzene, from which about 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is about 1.0
 5 milliliters/minute, unit operating temperature is about 140°C and the injection size is about 100 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent
 10 polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968, the disclosure of which is incorporated herein by reference) to derive the following equation:

$$15 \quad M_{\text{polyethylene}} = a + (M_{\text{polystyrene}})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the following formula: $M_j = (\sum w_i (M_i^j))^j$; where w_i is the weight fraction of the molecules with molecular weight M_i eluting from the GPC column in fraction
 20 i and $j = 1$ when calculating M_w and $j = -1$ when calculating M_n .

The M_w/M_n of the inventive ethylene interpolymer can be characterized as satisfying the following inequality:

$$1.25 \times \log M_w - 2.5 \leq M_w/M_n \leq 3.5 \times \log M_w - 11$$

and is in the range from 2.5 to 10.

25 The cross fraction chromatography (CFC) of the ethylene interpolymer of the present invention is conducted using a CFC T-150A unit which is manufactured and sold by Mitsubishi Kagaku Corp., Japan. Determinations by CFC is conducted as follows: a 20 milligrams of a sample is dissolved in 20 milliliters of dichlorobenzene at a temperature of 140°C to obtain a
 30 solution of the sample. Then, 5 ml of the solution is added to a temperature rising elution fractionation (TREF) column filled with glass beads and the solution permitted to cool to 0°C at a rate of $1^\circ\text{C}/\text{min}$. After cooling to 0°C , the solution is then heated so as to elevate the temperature of the solution at a rate of $1^\circ\text{C}/\text{min}$. and thereby extract

interpolymer fractions. Then, the extracted interpolymer fractions are subjected to gel permeation chromatography (GPC) using a Shodex AD806MS GPC column (which is manufactured and sold by Showa Denko K.K., Japan), followed by Fourier Transform Infrared Spectroscopy (FT-IR) using a
5 Nicolet Manga - IR Spectrometer 550 (which is manufactured and sold by Nicolet Co., Ltd., U.S.A.).

With respect to further details of the method for conducting CFC, reference can be made to the catalogue attached to the above-mentioned CFC T-150A.

10 With respect to conventional ethylene copolymers produced using a conventional Ziegler catalyst, the SCF is generally almost 0 or of a positive value. With respect to conventional ethylene copolymers produced using conventional metallocene catalysts which have recently been being put into practical use, the SCF is almost 0.

15 To determine the slope of cross-fractionation (SCF) of the ethylene interpolymer of the present invention, the relationship between an arbitrary temperature, $T(^{\circ}\text{C})$, and a molecular weight point on the molecular weight distribution profile of an interpolymer fraction extracted at the arbitrary temperature, $T(^{\circ}\text{C})$, is treated by the least
20 squares method to obtain a straight line. This straight line will have a slope (dimensionless) within the range defined by the formula:

$$\text{slope of cross-fractionation} = [\log M_p(T^1) - \log M_p(T^2)] / (T^1 - T^2)$$

where the arbitrary temperature, $T(^{\circ}\text{C})$, is any temperature at which extraction may be conducted which falls within the temperature range of
25 between a first temperature and a second temperature. The first temperature is the temperature at which a maximum amount of extraction is exhibited for the interpolymer, as determinable using cross-fractionation chromatography. The second temperature is the lower of a temperature which is 10°C higher than the first temperature or 96°C . The molecular
30 weight point is the point on the molecular weight distribution profile where the interpolymer fraction shows a peak having a maximum intensity. T^1 and T^2 are two different arbitrary extraction temperatures (in $^{\circ}\text{C}$) within the range of between the first temperature and the second

temperature. $M_p(T^1)$ and $M_p(T^2)$ are molecular weights corresponding to T^1 and T^2 , respectively, on the straight line.

For interpolymer fractions, the amount of which are less than 1 percent by weight (based on the total amount of interpolymer fractions extracted at the overall temperature range in CFC, excluding purge), are to be excluded from the least squares determination of the straight line.

FIG. 1 is a CFC contour plot of extraction temperature, molecular weight and molecular weight distribution for an interpolymer having a first temperature at about 66°C and a second temperature at about 76°C. The least squares straight line for the interpolymer is also included on the plot.

For the inventive interpolymers, the SCF will be negative. This means that the interpolymer fraction extracted at a low temperature (that is, a low density interpolymer fraction having a high comonomer content) will have a higher molecular weight than that of the interpolymer fraction extracted at a high temperature (that is, a high density interpolymer fraction having a low comonomer content). Also, a negative SFC indicates that for the present inventive ethylene interpolymer an interpolymer fraction having a high comonomer content has a high molecular weight. This characteristic (referred to herein as a "reverse comonomer distribution") is contrary to conventional ethylene copolymers in which interpolymer fractions having a high comonomer content typically have a low molecular weight.

Further, the ethylene copolymer of the present invention has a SCF within the range of from -0.005 to -1. This SCF range indicates that interpolymers having interpolymer fractions of widely varied comonomer contents and molecular weights can be obtained, wherein the interpolymer fractions vary from a low molecular weight interpolymer fraction having a low comonomer content (that is, high density interpolymer fractions having a low molecular weight) to a high molecular weight interpolymer fraction having a high comonomer content (that is, a low density copolymer fraction having a high molecular weight). As such, inventive interpolymers which have different comonomer contents, exhibit excellent miscibility with respect to each other or one another. Therefore, in the present invention, the interpolymers having different comonomer contents can be

readily blended, so as to obtain an interpolymer having desired properties, without the occurrence of gel formation.

When the slope of cross-fractionation (SCF) becomes too small, it becomes difficult to obtain a designed interpolymer having the desired structure and properties. Therefore, in the present invention, the SCF must be -1 or more, preferably in the range of from -0.5 to -0.007, more preferably in the range of from -0.1 to -0.01, and most preferably in the range of from -0.08 to -0.02.

When the inventive ethylene interpolymer is analyzed using CFC, the interpolymer shows characteristics such that the sum of the respective amounts of interpolymer fractions extracted at temperatures which are at least 10°C lower than the first temperature (as defined above) is less than 8 percent by weight, preferably less than or equal to 6 percent by weight, more preferably less than or equal to 4 percent by weight, and most preferably less than or equal to 2 percent by weight, based on the total amount of fractions extracted at temperatures in the overall range of extraction temperatures in CFC, excluding purge. In the present invention, the "sum of extractives at reduced temperatures" (SERT) can be obtained from an integral curve showing the amounts of extracted fractions relative to extraction temperatures. FIG. 2 is a CFC integral curve of the amount extracted relative to extraction temperature for an interpolymer having a first temperature at about 66°C.

While the inventive interpolymer will have a SERT of less than 8 percent by weight, conventional ethylene interpolymers, produced using a Ziegler-Natta catalyst system show characteristics such that a relatively large amount of interpolymer fractions are extracted at temperatures which are at least 10°C lower than the first temperature. These large SERT values indicate that conventional ethylene interpolymers have broad compositional distributions and contain low molecular weight waxy components or extremely low density copolymer fractions.

Conventionally, it has been considered that the ethylene interpolymers produced using metallocene catalysts, which have recently been put into practical use, have a narrow distribution in comonomer content. But when some of such ethylene copolymers are subjected to CFC measurement, a considerably large amount of interpolymer fractions are

extracted within a wide range of temperatures which are at least 10°C lower than the first temperature as defined above.

In comparison, due to such an extremely small content of fractions extracted at temperatures which are at least 10°C lower than the first temperature, the inventive ethylene interpolymer exhibits excellent properties which include no adverse effects associated with the presence of waxy components and low density copolymer fractions (for example, no or reduced smoking during high temperature extrusions). Further, in the present invention, it is possible to produce copolymers having a very low density and a very low molecular weight. Such copolymers can be advantageously mixed to provide a wide variety of mixtures, each comprising two or more different interpolymer components having different comonomer contents. Therefore, it becomes possible to design various mixtures having desired properties by the use of inventive interpolymers having a very low density and a very low molecular weight.

In the present invention, within a range in molecular weight of the ethylene copolymer which is defined by the formula (I):

$$\log (M_t) - \log (M_c) \leq 0.5 \quad (I)$$

wherein:

M_t is a molecular weight point on a molecular weight distribution profile at which the profile shows a peak having a maximum intensity, and
M_c is an arbitrary molecular weight point on the molecular weight distribution profile,
the molecular weight distribution profile being obtained together with a comonomer content distribution profile by subjecting the ethylene interpolymer to gel permeation chromatography/Fourier transformation infrared spectroscopy (GPC/FT-IR),
an approximate straight line obtained from the comonomer content distribution profile by the least squares method has a slope of molecular weight to comonomer distribution (SMWCD) defined by the formula (II):

$$SMWCD = [C(M_c^1) - C(M_c^2)] / (\log M_c^1 - \log M_c^2) \quad (II)$$

wherein:

Mc¹ and Mc² are two different arbitrary molecular weight points (Mc) which satisfy formula (I), and

C(Mc¹) and C(Mc²) are, respectively, comonomer contents.

corresponding to Mc¹ and Mc² on the approximate straight line.

Determination of the slope of molecular weight to comonomer distribution is obtained using gel permeation chromatography/Fourier transformation infrared spectroscopy (GPC/FT-IR). For this determination, the GPC measurement is conducted using a 150C ALC/GPC unit manufactured and sold by Waters Assoc. Co. USA., in which three columns (one Shodex AT-807S manufactured and sold by Showa Denko K.K., Japan and two TSK-GEL GMH-H6 manufactured and sold by Tosoh Corp., Japan), connected in series, are used. The FT-IR measurement is conducted by dissolving 20 to 30 mg of a sample in 15 ml of trichlorobenzene at a temperature of 140°C, and applying 500 to 1,000μl of the resultant solution to a FT-IR apparatus (Perkin-Elmer 1760X, manufactured and sold by Perkin Elmer Cetus, Co., Ltd., USA).

The comonomer content is defined as a value obtained by dividing the number of comonomer units relative to 1,000 methylene units contained in the interpolymer by 1000. For example, when 5 comonomer units are contained in the interpolymer relative to 1000 methylene units, the comonomer content is 0.005. The value of the comonomer content can be obtained using FT-IR and is derived from the ratio of the intensity of an absorbance attributed to the comonomer units to the intensity of an absorbance attributed to the methylene units. For example, when a linear α-olefin is used as a comonomer, the ratio of the intensity of absorbance at 2960 cm⁻¹, which is attributed to the methyl groups, to the intensity of absorbance at 2925 cm⁻¹, which is attributed to the methylene groups, is obtained by FT-IR. From this ratio, the comonomer content derived.

Generally, the comonomer content distribution profile is shown as a line containing points indicating comonomer contents. For improving the accuracy of the profile, it is desirable to obtain a large number of points indicating the comonomer contents by repeatedly conducting the comonomer content measurement using the same sample under the same conditions. FIG. 3 is a plot of the molecular weight and comonomer content distribution for an

interpolymer wherein an approximate straight line is included. The SMWCD of the inventive interpolymer will be in the range from 0.005 to 0.05.

The inventive interpolymer can also be defined with reference to its short chain branching distribution and/or partitioning factors. In particular, the short chain branching distribution of the interpolymer can be examined by several techniques, such as, for example, ATREF-DV and GPC-FTIR. If the material of the interpolymer is divided into portions starting at one end of the distribution or the other, the relationship between high short chain branching content due to high comonomer content and molecular weight can be determined.

The inventive interpolymer can be characterized as having a molecular weight maximum which occurs in that 50 percent by weight of the composition which has the highest weight percent comonomer content.

With reference to partitioning factors, the inventive interpolymer is characterized as having a comonomer partitioning factor C_{pf} which is equal to or greater than 1.10 or a molecular weight partitioning factor M_{pf} which is equal to or greater than 1.15, or a comonomer partitioning factor C_{pf} which is equal to or greater than 1.10 and a molecular weight partitioning factor M_{pf} which is equal to or greater than 1.15, where the comonomer partitioning factor C_{pf} is calculated from the equation:

$$C_{pf} = \frac{\frac{\sum_{i=1}^n w_i c_i}{\sum_{i=1}^n w_i}}{\frac{\sum_{j=1}^m w_j c_j}{\sum_{j=1}^m w_j}}$$

where c_i is the mole fraction comonomer content and w_i is the normalized weight fraction as determined by GPC/FTIR for the n FTIR data points above the median molecular weight, c_j is the mole fraction comonomer content and w_j is the normalized weight fraction as determined by GPC/FTIR for the m FTIR data points below the median molecular weight, wherein only those weight fractions w_i or w_j which have associated mole

fraction comonomer content values are used to calculate C_{pf} and n and m are greater than or equal to 3; and where the molecular weight partitioning factor M_{pf} is calculated from the equation:

$$M_{pf} = \frac{\frac{\sum_{i=1}^n w_i \cdot M_i}{\sum_{i=1}^n w_i}}{\frac{\sum_{j=1}^m w_j \cdot M_j}{\sum_{j=1}^m w_j}}$$

5 where M_i is the viscosity average molecular weight and w_i is the normalized weight fraction as determined by ATREF-DV for the n data points in the fractions below the median elution temperature, M_j is the viscosity average molecular weight and w_j is the normalized weight fraction as determined by ATREF-DV for the m data points in the fractions above the
10 median elution temperature, wherein only those weight fractions, w_i or w_j which have associated viscosity average molecular weights greater than zero are used to calculate M_{pf} and n and m are greater than or equal to 3.

15 In another embodiment, the interpolymer is characterized as having a molecular weight partitioning factor, M_{pf} , desirably equal to or greater than 1.15, more desirably is equal to or greater than 1.30, even more desirably is equal to or greater than 1.40, preferably is equal to or greater than 1.50, more preferably is equal to or greater than 1.60, even more preferably is equal to or greater than 1.70.

20 ATREF-DV has been described in U.S. Patent No. 4,798,081 and in "Determination of Short-Chain Branching Distributions of Ethylene copolymers by Automated Analytical Temperature Rising Elution Fractionation" (Auto-ATREF), J. of Appl Pol Sci: Applied Polymer Symposium 45, 25-37 (1990). ATREF-DV is a dual detector analytical system that is capable of fractionating semi-crystalline polymers like Linear Low
25 Density Polyethylene (LLDPE) as a function of crystallization temperature while simultaneously estimating the molecular weight of the fractions. With regard to the fractionation, ATREF-DV is analogous to Temperature Rising Elution Fractionation (TREF) analysis that have been published in the open literature over the past 15 years. The primary difference is

that this Analytical - TREF (ATREF) technique is done on a small scale and fractions are not actually isolated. Instead, a typical liquid chromatographic (LC) mass detector, such as an infrared single frequency detector, is used to quantify the crystallinity distribution as a function of elution temperature. This distribution can then be transformed to any number of alternative domains such as short branching frequency, comonomer distribution, or possibly density. Thus, this transformed distribution can then be interpreted according to some structural variable like comonomer content, although routine use of ATREF for comparisons of various LLDPE's is often done directly in the elution temperature domain.

To obtain ATREF-DV data, a commercially available viscometer especially adapted for LC analysis, such as a Viskotek™ is coupled with the IR mass detector. Together these two LC detectors can be used to calculate the intrinsic viscosity of the ATREF-DV eluant. The viscosity average molecular weight of a given fraction can then be estimated using appropriate Mark Houwink constants, the corresponding intrinsic viscosity, and suitable coefficients to estimate the fractions concentration (dl/g) as it passes through the detectors. Thus, a typical ATREF-DV report will provide the weight fraction polymer and viscosity average molecular weight as a function of elution temperature. M_{pf} is then calculated using the equation given.

The molecular weight partitioning factor M_{pf} is calculated from ATREF/DV data. It characterizes the ratio of the average molecular weight of the fractions with high comonomer content to the average molecular weight of the fractions with low comonomer content. Higher and lower comonomer content are defined as being below or above the median elution temperature of the ATREF concentration plot respectively, that is, the ATREF data is divided into two parts of equal weight.

The inventive ethylene homopolymer and interpolymer are characterized as having long chain branching. Long chain branching is defined herein as a chain length of at least one carbon more than two carbons less than the total number of carbons in the comonomer, for example, the long chain branch of an ethylene/octene substantially linear ethylene interpolymer is at least seven (7) carbons in length (that is, 8 carbons less 2 equals 6 carbons plus one equals seven carbons long chain

branch length). The long chain branch can be as long as about the same length as the length of the polymer back-bone. Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method of Randall (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297). Long chain branching, of course, is to be distinguished from short chain branches which result solely from incorporation of the comonomer, so for example the short chain branch of an ethylene/octene substantially linear polymer is six carbons in length, while the long chain branch for that same polymer is at least seven
10 carbons in length.

Long chain branching can be distinguished from short chain branching by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, for example for ethylene homopolymers, it can be quantified using the method of Randall, (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297). However as a practical matter, current ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of about six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as
20 about the same length as the length of the polymer backbone.

Although conventional ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms, there are other known techniques useful for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. For example, U.S. Patent No. 4,500,648 teaches that long chain branching frequency (LCB) can be represented by the equation $\text{LCB} = b/M_w$ wherein b is the weight average number of long chain branches per molecule and M_w is the weight average molecular weight. The molecular weight averages and the long chain
30 branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods, respectively.

Two other useful methods for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers are gel permeation chromatography coupled with a low angle
35 laser light scattering detector (GPC-LALLS) and gel permeation

chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, for example, Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is indeed a useful technique for quantifying the presence of long chain branches in ethylene polymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using ^{13}C NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify the level of long chain branches in ethylene polymers.

The polymer backbone of the inventive ethylene polymer is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons.

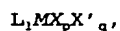
The inventive ethylene polymer may also be defined with reference to its resistance to the onset of melt fracture as determined in gas extrusion rheology tests and as is described herein below with regard to substantially linear ethylene polymers. That is, the inventive ethylene polymer can be defined as having a critical shear rate at onset of surface melt fracture which is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a comparative linear

ethylene polymer that does not contain long chain branching but has about the same I_2 and M_w/M_n , wherein "about the same" as used herein means that each value is within 10 percent of the comparative value of the comparative linear ethylene polymer. Or, alternately, the inventive
5 ethylene polymer may be defined as having a critical shear stress at the onset of gross melt fracture and critical shear stress at the onset of surface melt fracture of greater than 4×10^6 dyne/cm², and greater than 2.8×10^6 dyne/cm², respectively

The ethylene polymers of the present invention can be produced under
10 slurry process conditions with the supported constrained geometry catalysts as described hereinafter.

The preferred catalyst systems to be used in the present invention comprise a constrained geometry catalyst (a) and a solid component (b).

Exemplary single site catalysts comprise a transition metal complex
15 corresponding to the formula:



that has been or subsequently is rendered catalytically active by combination with an activating cocatalyst or by use of an activating technique, wherein;

20 M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4, bound in an η^5 bonding mode to one or more L groups;

L independently each occurrence is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or
25 octahydrofluorenyl- group optionally substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, aminohydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, dihydrocarbylphosphino, silyl, aminosilyl, hydrocarbyloxysilyl, and halosilyl groups containing up to 20 non-hydrogen
30 atoms, or further optionally two such L groups may be joined together by a divalent substituent selected from hydrocarbadiyl, halohydrocarbadiyl, hydrocarbyleneoxy, hydrocarbyleneamino, siladiyl, halosiladiyl, and divalent aminosilane, groups containing up to 20 non-hydrogen atoms;

X independently each occurrence is a monovalent anionic σ -bonded ligand group, a divalent anionic σ -bonded ligand group having both valences bonded to M, or a divalent anionic σ -bonded ligand group having one valency bonded to M and one valency bonded to an L group, said X
5 containing up to 60 nonhydrogen atoms;

X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

l is one or two;

p is 0, 1 or 2, and is 1 less than the formal oxidation state of M when X
10 is an monovalent anionic σ -bonded ligand group or a divalent anionic σ -bonded ligand group having one valency bonded to M and one valency bonded to an L group, or p is 1 +1 less than the formal oxidation state of M when X is a divalent anionic σ -bonded ligand group having both valencies bonded to M; and

15 q is 0, 1 or 2.

Single site catalysts including the constrained geometry catalysts are believed to exist in the form of a mixture of one or more cationic or zwitterionic species derived from the metallocene-based transition metal coordination complexes in combination with an activating compound. Fully
20 cationic or partially charge separated metal complexes, that is, zwitterionic metal complexes, have been previously disclosed in U.S. Patent Nos. 5,470,993 and 5,486,632.

The cationic complexes of single site catalysts are believed to correspond to the formula:

25
$$L_l M^+ X_{p-1} A^-$$

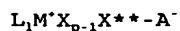
wherein:

M is a Group 4 metal in the +4 or +3 formal oxidation state;

L, X, l and p are as previously defined; and

A⁻ is a noncoordinating, compatible anion derived from the
30 activating cocatalyst.

The zwitterionic complexes in particular result from activation of a Group 4 metal diene complex that is in the form of a metallocyclopentene, wherein the metal is in the +4 formal oxidation state, (that is, X is 2-butene-1,4-diyl, or a hydrocarbyl substituted derivative thereof, having both valencies bonded to M) by the use of a Lewis acid activating cocatalyst, especially tris(perfluoro-aryl)boranes. These zwitterionic complexes are believed to correspond to the formula:



wherein:

10 M is a Group 4 metal in the +4 formal oxidation state;

L, X, 1 and p are as previously defined;

X** is the divalent remnant of the conjugated diene, X', formed by ring opening at one of the carbon to metal bonds of a metallocyclopentene; and

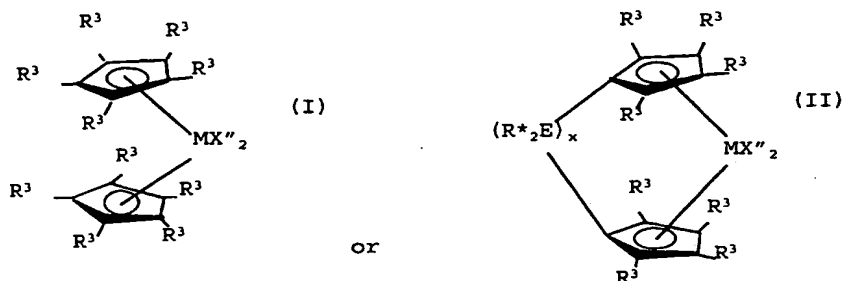
15 A⁻ is a noncoordinating, compatible anion derived from the activating cocatalyst.

As used herein, the recitation "noncoordinating" means an anion which either does not coordinate to the transition metal component or which is only weakly coordinated therewith remaining sufficiently labile to be displaced by a neutral Lewis base, including an α -olefin. A non-coordinating anion specifically refers to an anion which when functioning as a charge balancing anion in the catalyst system of this invention, does not transfer a fragment thereof to said cation thereby forming a neutral four coordinate metal complex and a neutral byproduct. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerizations.

Preferred X' groups are phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR)₃, wherein R is as previously defined; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine, tetramethyl-ethylenediamine (TMEDA), and triethylamine;

olefins; and conjugated dienes having from 4 to 40 carbon atoms. Complexes including conjugated diene X' groups include those wherein the metal is in the +2 formal oxidation state.

5 Examples of coordination complexes used for single site catalyst preparation include the foregoing species:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

10 R^3 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbonyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring
15 system,

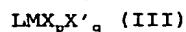
X'' independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X'' groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms forming a π -complex with M,
20 whereupon M is in the +2 formal oxidation state,

R^* independently each occurrence is C_{1-4} alkyl or phenyl,

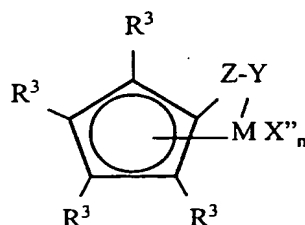
E independently each occurrence is carbon or silicon, and

x is an integer from 1 to 8.

Additional examples of metal coordination complexes including the constrained geometry catalysts include those corresponding to the formula:



wherein L, M, X, X', p and q are as previously defined. A preferred metal complex belongs to the foregoing class (III) and corresponds to the formula:



wherein:

M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

R³ in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R³ having up to 20 non-hydrogen atoms, or adjacent R³ groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

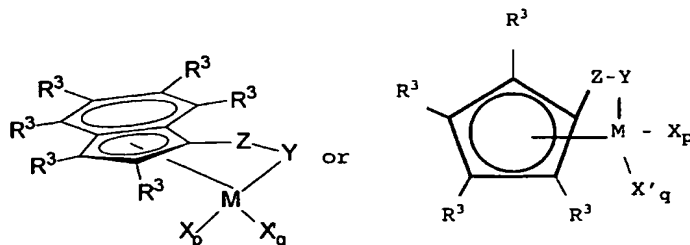
each X'' is a halo, hydrocarbyl, hydrocarbyloxy, hydrocarbylamino, or silyl group, said group having up to 20 non-hydrogen atoms, or two X'' groups together form a neutral C₅₋₃₀ conjugated diene or a divalent derivative thereof;

Y is -O-, -S-, -NR*- , -PR*-;

Z is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, or GeR*₂, wherein R* is as previously defined, and

n is an integer from 1 to 3.

Most preferred coordination complexes used according to the present invention are complexes corresponding to the formula:



wherein:

- 5 R^3 independently each occurrence is a group selected from hydrogen, hydrocarbyl, halohydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to 20 nonhydrogen atoms;

M is titanium, zirconium or hafnium;

Z, Y, X and X' are as previously defined;

- 10 p is 0, 1 or 2; and

q is zero or one;

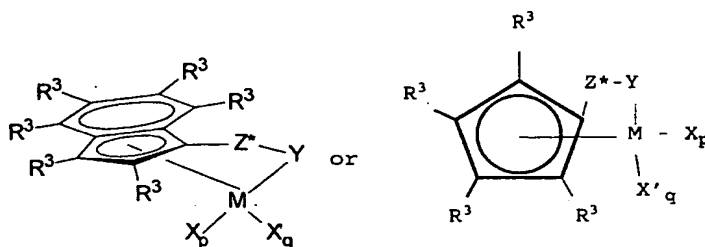
with the proviso that:

- when p is 2, q is zero, M is in the +4 formal oxidation state, and X is an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy- and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 20 nonhydrogen atoms,

- 20 when p is 1, q is zero, M is in the +3 formal oxidation state, and X is a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N-dimethylaminomethyl)phenyl, and 2-(N,N-dimethyl)-aminobenzyl, or M is in the +4 formal oxidation state, and X is a divalent derivative of a conjugated diene, M and X together forming a
25 metallocyclopentene group, and

when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M.

- 5 More preferred coordination complexes used according to the present invention are complexes corresponding to the formula:



wherein:

R³ independently each occurrence is hydrogen or C₁₋₆ alkyl;

10 M is titanium;

Y is -O-, -S-, -NR*- , -PR*-;

Z* is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, or GeR*₂;

15 R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 20 non-hydrogen atoms, and optionally, two R* groups from Z (when R* is not hydrogen), or an R* group from Z and an R* group from Y form a ring system;

p is 0, 1 or 2;

q is zero or one;

20 with the proviso that:

when p is 2, q is zero, M is in the +4 formal oxidation state, and X is independently each occurrence methyl or benzyl,

when p is 1, q is zero, M is in the +3 formal oxidation state, and X is 2-(N,N-dimethyl)aminobenzyl; or M is in the +4 formal oxidation state and X is 2-butene-1,4-diyl, and

5 when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene. The latter diene is illustrative of unsymmetrical diene groups that result in production of metal complexes that are actually mixtures of the respective geometrical isomers.

10 The complexes can be prepared by use of well known synthetic techniques. A preferred process for preparing the metal complexes is disclosed in USSN 8/427,378, filed April 24, 1995. The reactions are conducted in a suitable noninterfering solvent at a temperature from -100 to 300 °C, preferably from -78 to 100 °C, most preferably from 0 to 50 °C. A reducing agent may be used to cause the metal M, to be reduced from a
15 higher to a lower oxidation state. Examples of suitable reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy, sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienylys, and Grignard reagents.

20 Suitable reaction media for the formation of the complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane,
25 methylcyclohexane, methylcycloheptane, and mixtures thereof; aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C₁₋₄ dialkyl ethers, C₁₋₄ dialkyl ether derivatives of (poly)alkylene glycols, and tetrahydrofuran. Mixtures of the foregoing are also suitable.

30 In the preferred catalyst systems to be used in the present invention, the active species of the catalyst is strongly associated with a carrier, so that the active species of the catalyst is not liberated from the carrier and does not escape from the polymer being produced.

35 (b) The Solid Component

Specifically stated, in one preferred supported catalyst component to be used in the process of the present invention, an active hydrogen moiety of an activator compound for the transition metal component, may be bonded to the hydroxyl groups of the support material through an organometal compound. That is, the activator compound is strongly associated with the support material. Such supported catalyst components are more fully described in WO 96/28480.

In a further preferred supported catalyst component to be used in the present invention aluminosilicate is fixed to the support material by a heating and/or washing treatment, such that the aluminosilicate is substantially not extractable under severe conditions (toluene at 90 °C). Such supported catalyst components are more fully described in WO 96/16092.

Suitable support materials for use in the present invention include porous resinous materials, for example, polyolefins such as polyethylenes and polypropylenes or copolymers of styrene-divinylbenzene, and solid inorganic oxides including oxides of Group 2, 3, 4, 13, or 14 metals, such as silica, alumina, magnesium oxide, titanium oxide, thorium oxide, as well as mixed oxides of silica. Suitable mixed oxides of silica include those of silica and one or more Group 2 or 13 metal oxides, such as silica-magnesia or silica-alumina mixed oxides. Silica, alumina, and mixed oxides of silica and one or more Group 2 or 13 metal oxides are preferred support materials. Preferred examples of such mixed oxides are the silica-aluminas. The most preferred support material is silica. The shape of the silica particles is not critical and the silica may be in granular, spherical, agglomerated, fumed or other form. Suitable silicas include those that are available from Grace Davison (division of W.R. Grace & Co.) under the designations SD 3216.30, SP-9-10046, Davison Syloid™ 245, Davison 948 and Davison 952, from Degussa AG under the designation Aerosil 812, and from Crossfield under the designation ES 70X.

Support materials suitable for the present invention preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m²/g, and preferably from 100 to 600 m²/g. The pore volume of the support, as determined by nitrogen adsorption, is typically up to 5 cm³/g, advantageously between 0.1 and 3 cm³/g,

preferably from 0.2 to 2 cm³/g. The average particle size is not critical but typically is from 0.5 to 500 μm, preferably from 1 to 200 μm, more preferably to 100 μm.

The support material may be subjected to a heat treatment and/or
5 chemical treatment to reduce the water content or the hydroxyl content of the support material. Both dehydrated support materials and support materials containing small amounts of water can be used. Typical thermal pretreatments are carried out at a temperature from 30°C to 1000°C for a duration of 10 minutes to 50 hours in an inert atmosphere or under reduced
10 pressure. Typical support materials have a surface hydroxyl content of from 0.1 micromol, preferably from 5 micromol, more preferably from 0.05 mmol to not more than 10 mmol and preferably not more than 5 mmol hydroxyl groups per g of solid support, more preferably from 0.5 to 2 mmol per gram. The hydroxyl content can be determined by known techniques, such as
15 infrared spectroscopy and titration techniques using a metal alkyl or metal hydroxide, for example, adding an excess of dialkyl magnesium to a slurry of the solid support and determining the amount of dialkyl magnesium remaining in solution via known techniques. This latter method is based on the reaction of $S-OH + MgR_2 \rightarrow S-OMgR + RH$, wherein S is the
20 solid support.

As an alternative technique for measuring the amount of hydroxyl groups on the surface of the inorganic solid, a method comprising the following procedures can be mentioned. Illustratively stated, the inorganic solid is dried in a nitrogen gas flow at 250 °C for 10 hours and
25 then, the weight of the dried inorganic solid is measured and taken as an initial weight represented by "W1" (unit: g). After this, the dried inorganic solid is heated to 1,000 °C and then, allowed to cool to the room temperature. The weight of the cooled inorganic solid is measured, and the difference between the initial weight (W1) and the weight of the
30 cooled inorganic solid is determined and taken as a weight loss represented by "ΔW" (unit: g). The amount of the hydroxyl groups is calculated by the following formula:

$$\text{Amount of the hydroxyl groups} = (1,000 \times \Delta W / 18.02) / W1 \text{ mmol/g.}$$

It is preferred that the inorganic solid having hydroxyl groups on the surface thereof to be used in the method of the present invention do not contain water such as crystal water or adsorbed water. Any water contained in the inorganic solid can be removed therefrom by heating in a nitrogen atmosphere or under reduced pressure at 250 °C or more for 1 hour or more.

According to one preferred embodiment, the solid (or supported) catalyst comprises a supported catalyst component comprising (a) a support material, an organometal compound wherein the metal is selected from Groups 2-13 of the Periodic Table of the Elements, germanium, tin, and lead, and (b) an activator compound comprising (b-1) a cation which is capable of reacting with a transition metal compound to form a catalytically active transition metal complex, and (b-2) a compatible anion having up to 100 nonhydrogen atoms and containing at least one substituent comprising an active hydrogen moiety; and a transition metal compound.

The support material is typically treated with the organometal compound. Suitable organometal compounds are those comprising metals of Groups 2-13, germanium, tin, and lead, and at least two substituents selected from hydride, hydrocarbyl radicals, trihydrocarbyl silyl radicals, and trihydrocarbyl germyl radicals. Additional substituents preferably comprise one or more substituents selected from hydride, hydrocarbyl radicals, trihydrocarbyl substituted silyl radicals, trihydrocarbyl substituted germyl radicals, and hydrocarbyl-, trihydrocarbyl silyl- or trihydrocarbyl germyl-substituted metalloid radicals.

The recitation "metalloid", as used herein, includes non-metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Examples of such organometal compounds include organomagnesium, organozinc, organoboron, organoaluminum, organogermanium, organotin, and organolead compounds, and mixtures thereof. Further suitable organometal compounds are alumoxanes. Preferred examples are alumoxanes and compounds represented by the following formulae: MgR^1_2 , ZnR^1_2 , $BR^1_xR^2_y$, $AlR^1_xR^2_y$, wherein R^1 independently each occurrence is hydride, a hydrocarbyl

radical, a trihydrocarbyl silyl radical, a trihydrocarbyl germyl radical, or a trihydrocarbyl-, trihydrocarbyl silyl-, or trihydrocarbyl germyl-substituted metalloid radical, R^2 independently is the same as R^1 , x is 2 or 3, y is 0 or 1 and the sum of x and y is 3, and mixtures thereof.

- 5 Examples of suitable hydrocarbyl moieties are those having from 1 to 20 carbon atoms in the hydrocarbyl portion thereof, such as alkyl, aryl, alkaryl, or aralkyl. Preferred radicals include methyl, ethyl, *n*- or *i*-propyl, *n*-, *s*- or *t*-butyl, phenyl, and benzyl. Preferably, the aluminum component is selected from the group consisting of alumoxane and aluminum
- 10 compounds of the formula AlR^1_x wherein R^1 in each occurrence independently is hydride or a hydrocarbyl radical having from 1 to 20 carbon atoms, and x is 3. Suitable trihydrocarbyl aluminum compounds are trialkyl or triaryl aluminum compounds wherein each alkyl or aryl group has from 1 to 10 carbon atoms, or mixtures thereof, and preferably trialkyl aluminum
- 15 compounds such as trimethyl, triethyl, tri-isobutyl aluminum.

Alumoxanes (also referred to as aluminoxanes) are oligomeric or polymeric aluminum oxy compounds containing chains of alternating aluminum and oxygen atoms, whereby the aluminum carries a substituent, preferably an alkyl group. The structure of alumoxane is believed to be represented

20 by the following general formulae $(-Al(R)-O)_m$, for a cyclic alumoxane, and $R_2Al-O(-Al(R)-O)_m-AlR_2$, for a linear compound, wherein R independently in each occurrence is a C_1 - C_{10} hydrocarbyl, preferably alkyl, or halide and m is an integer ranging from 1 to 50, preferably at least 4. Alumoxanes are typically the reaction products of water and an aluminum alkyl, which in

25 addition to an alkyl group may contain halide or alkoxide groups. Reacting several different aluminum alkyl compounds, such as, for example, trimethyl aluminum and tri-isobutyl aluminum, with water yields so-called modified or mixed alumoxanes. Preferred alumoxanes are methylalumoxane and methylalumoxane modified with minor amounts of other lower alkyl

30 groups such as isobutyl. Alumoxanes generally contain minor to substantial amounts of starting aluminum alkyl compound.

The way in which the alumoxane is prepared is not critical. When prepared by the reaction between water and aluminum alkyl, the water may be combined with the aluminum alkyl in various forms, such as liquid,

35 vapor, or solid, for example in the form of crystallization water. Particular techniques for the preparation of alumoxane type compounds by

contacting an aluminum alkyl compound with an inorganic salt containing water of crystallization are disclosed in U.S. Patent 4,542,199. In a particular preferred embodiment an aluminum alkyl compound is contacted with a regeneratable water-containing substance such as hydrated alumina, silica or other substance. This is disclosed in European Patent Application No. 338,044.

The supported catalyst according to this embodiment generally comprise a support material combined or treated with the organometal compound and containing at least 0.1 micromol of organometal compound per g of support material, typically at least 5 micromole per g support material, advantageously at least 0.5 weight percent of the metal, preferably aluminum, expressed in gram of metal atoms per g of support material. Preferably, the amount of metal is at least 2 weight percent, and generally not more than 40 weight percent, and more preferably not more than 30 weight percent. At too high amounts of metal the supported catalyst becomes expensive. At too low amounts the catalyst efficiency goes down to drop below acceptable levels.

The supported catalyst preferably contain a treated support material (a) comprising a support material and an alumoxane wherein not more than 10 percent aluminum present in the treated support material is extractable in a one hour extraction with toluene of 90°C using 10 mL toluene per gram of pretreated support material. More preferably, not more than 9 percent aluminum present in the supported catalyst component is extractable, and most preferably not more than 8 percent. This is especially advantageous when the supported catalyst is used in a polymerization process where a diluent or solvent is used which may extract non-fixed alumoxane from the support material. It has been found that when the amount of extractables is below the levels given above, the amount of alumoxane that can diffuse into the polymerization solvent or diluent, if used, is so low that no appreciable amount of polymer will be formed in the diluent, as compared to polymer formed on the support material. If too much polymer is formed in the diluent the polymer bulk density will decrease below acceptable levels and reactor fouling problems may occur.

The toluene extraction test is carried out as follows: About 1 g of supported catalyst component or supported catalyst, with a known aluminum content, is added to 10 mL toluene and the mixture is then heated to 90°C

under an inert atmosphere. The suspension is stirred well at this temperature for 1 hour. Then the suspension is filtered applying reduced pressure to assist in the filtration step. The solids are washed twice with 3 to 5 mL toluene of 90°C per gram of solids. The solids are then
5 dried at 120°C for 1 hour, and subsequently the aluminum content of the solids is measured. The difference between the initial aluminum content and the aluminum content after the extraction divided by the initial aluminum content and multiplied by 100 percent, gives the amount of extractable aluminum.

10 The aluminum content can be determined by slurrying about 0.5 g of supported catalyst component or supported catalyst in 10 mL hexane. The slurry is treated with 10 to 15 mL 6N sulfuric acid, followed by addition of a known excess of EDTA. The excess amount of EDTA is then back-titrated with zinc chloride.

15 Without wishing to be bound by any theory, it is believed that the activator compound according to this embodiment reacts with the organometal compound through the active hydrogen-containing substituent. It is believed that a group R^1 of the organometal compound combines with the active hydrogen moiety of the activator compound to release a neutral
20 organic compound, for example an alkane, or hydrogen gas thereby chemically coupling the metal atom with the activator compound residue. Thus the activator is believed to become chemically attached to the support material once the support material has been treated with the organometal compound or adduct of organometal compound and activator
25 compound. Upon addition of the transition metal compound a supported catalyst is formed having improved properties.

The activator compound useful in the present invention contains a compatible anion having up to 100, and preferably up to 50 nonhydrogen atoms and having at least one substituent comprising an active hydrogen
30 moiety. Preferred substituents comprising an active hydrogen moiety correspond to the formula (I):



wherein G is a polyvalent hydrocarbon radical, T is O, S, NR, or PR, wherein R is a hydrocarbyl radical, a trihydrocarbyl silyl radical, a

trihydrocarbyl germyl radical, or hydrogen, H is hydrogen, q is 0 or 1, and preferably 1, and r is an integer from 1 to 3, preferably 1.

Polyvalent hydrocarbon radical G has r+1 valencies, one valency being with a metal or metalloid of the Groups 5-15 of the Periodic Table of the

- 5 Elements in the compatible anion, the other valency or valencies of G being attached to r groups T-H. Preferred examples of G include divalent hydrocarbon radicals such as: alkylene, arylene, aralkylene, or alkarylene radicals containing from 1 to 20 carbon atoms, more preferably from 2 to 12 carbon atoms. Suitable examples of G include phenylene, biphenylene,
10 naphthylene, methylene, ethylene, 1,3-propylene, 1,4-butylene, phenylmethylene ($-C_6H_4-CH_2-$). The polyvalent hydrocarbyl portion G may be further substituted with radicals that do not interfere with the coupling function of the active hydrogen moiety. Preferred examples of such non-interfering substituents are alkyl, aryl, alkyl- or aryl-substituted silyl
15 and germyl radicals, and fluoro substituents.

- The group T-H in the previous formula thus may be an -OH, -SH, -NRH, or -PRH group, wherein R preferably is a C_{1-18} , preferably a C_{1-10} hydrocarbyl radical or hydrogen, and H is hydrogen. Preferred R groups are alkyls, cycloalkyls, aryls, arylalkyls, or alkylaryls of 1 to 18
20 carbon atoms, more preferably those of 1 to 12 carbon atoms. The -OH, -SH, -NRH, or -PRH groups may be part of a larger functionality such as, for example, $C(O)-OH$, $C(S)-SH$, $C(O)-NRH$, and $C(O)-PRH$. Most preferably, the group T-H is a hydroxy group, -OH, or an amino group, -NRH.

- Very preferred substituents $G_q(T-H)_r$ comprising an active hydrogen
25 moiety include hydroxy- and amino-substituted aryl, aralkyl, alkaryl or alkyl groups, and most preferred are the hydroxyphenyls, especially the 3- and 4-hydroxyphenyl groups, hydroxytolyls, hydroxy benzyls (hydroxymethylphenyl), hydroxybiphenyls, hydroxynaphthyls, hydroxycyclohexyls, hydroxymethyls, and hydroxypropyls, and the
30 corresponding amino-substituted groups, especially those substituted with -NRH wherein R is an alkyl or aryl radical having from 1 to 10 carbon atoms, such as for example methyl, ethyl, propyl, i-propyl, n-, i-, or t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl, phenyl, benzyl, tolyl, xylyl, naphthyl, and biphenyl.

The compatible anion containing the substituent which contains an active hydrogen moiety, may further comprise a single Group 5-15 element or a plurality of Group 5-15 elements, but is preferably a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is bulky. A compatible anion specifically refers to an anion which, when functioning as a charge balancing anion, does not transfer an anionic substituent or fragment thereof to the transition metal cation thereby forming a neutral transition metal compound and a neutral metal by-product. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerizations.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core carrying a substituent containing an active hydrogen moiety which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the transition metal cation) which is formed when the activator compound and transition metal compound are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals for the anions of activator compounds include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Activator compounds which contain anions comprising a coordination complex containing a single boron atom and a substituent comprising an active hydrogen moiety are preferred.

Preferably, compatible anions containing a substituent comprising an active hydrogen moiety may be represented by the following general formula (II):



wherein:

M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements;

Q independently in each occurrence is selected from the group consisting of hydride, dihydrocarbylamido, preferably dialkylamido,

halide, hydrocarbyloxy, preferably alkoxide and aryloxy, hydrocarbyl, and substituted-hydrocarbyl radicals, including halo-substituted hydrocarbyl radicals, and hydrocarbyl- and halo-hydrocarbyl-substituted organo-metalloid radicals, the hydrocarbyl portion having from 1 to 20 carbons with the proviso that in not more than one occurrence is Q halide;

G is a polyvalent hydrocarbon radical having r+1 valencies and preferably divalent hydrocarbon radical bonded to M' and T;

T is O, S, NR, or PR, wherein R is a hydrocarbon radical, a trihydrocarbyl silyl radical, a trihydrocarbyl germyl radical, or hydrogen;

m is an integer from 1 to 7, preferably 3;

n is an integer from 0 to 7, preferably 3;

q is an integer 0 or 1, preferably 1;

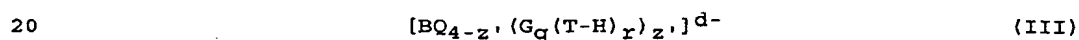
r is an integer from 1 to 3, preferably 1;

z is an integer from 1 to 8, preferably 1;

d is an integer from 1 to 7, preferably 1; and

$n+z-m = d$.

Preferred boron-containing anions which are particularly useful in this invention may be represented by the following general formula (III):



wherein:

B is boron in a valence state of 3;

z' is an integer from 1-4, preferably 1;

d is 1; and

Q, G, T, H, q, and r are as defined for formula (II). Preferably, z' is 1, q is 1, and r is 1.

Illustrative, but not limiting, examples of anions of activator compounds to be used in the present invention are boron-containing anions such as triphenyl(hydroxyphenyl)borate, diphenyl-di(hydroxyphenyl)borate,

triphenyl (2,4-dihydroxyphenyl)borate, tri(p-tolyl) - (hydroxyphenyl)borate, tris(pentafluorophenyl) (hydroxyphenyl)borate, tris-(2,4-dimethylphenyl) (hydroxyphenyl) borate, tris-(3,5-dimethylphenyl) (hydroxyphenyl)borate, tris-(3,5-di-
5 trifluoromethylphenyl) (hydroxyphenyl)borate, tris(pentafluorophenyl) (2-hydroxyethyl) borate, tris(pentafluorophenyl) (4-hydroxybutyl)borate, tris(pentafluorophenyl) (4-hydroxy- cyclohexyl)borate, tris(pentafluorophenyl) (4-(4'-hydroxyphenyl)phenyl)borate, tris(pentafluorophenyl) (6-hydroxy-2-naphthyl)borate, and the like. A
10 highly preferred activator complex is tris(pentafluorophenyl) (4-hydroxyphenyl)borate. Other preferred anions of activator compounds are those above mentioned borates wherein the hydroxy functionality is replaced by an amino NHR functionality wherein R preferably is methyl, ethyl, or t-butyl.

15 The cationic portion (b-1) of the activator compound to be used in association with the compatible anion (b-2) can be any cation which is capable of reacting with the transition metal compound to form a catalytically active transition metal complex, especially a cationic transition metal complex. The cations (b-1) and the anions (b-2) are used
20 in such ratios as to give a neutral activator compound. Preferably the cation is selected from the group comprising Brønsted acidic cations, carbonium cations, silylium cations, and cationic oxidizing agents.

Brønsted acidic cations may be represented by the following general formula:

25 $(L-H)^+$

wherein:

L is a neutral Lewis base, preferably a nitrogen, phosphorus, or sulfur containing Lewis base; and $(L-H)^+$ is a Brønsted acid. The Brønsted acidic cations are believed to react with the transition metal compound by
30 transfer of a proton of said cation, which proton combines with one of the ligands on the transition metal compound to release a neutral compound.

Illustrative, but not limiting, examples of Brønsted acidic cations of activator compounds to be used in the present invention are trialkyl-substituted ammonium cations such as triethylammonium, tripropylammonium,

tri(n-butyl)ammonium, trimethylammonium, tributylammonium, and tri(n-octyl)ammonium. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium, N,N-diethylanilinium, N,N-2,4,6-pentamethylanilinium, N,N-dimethylbenzylammonium and the like;

5 dialkylammonium cations such as di-(i-propyl)-ammonium, dicyclohexylammonium and the like; and triarylphosphonium cations such as triphenylphosphonium, tri(methylphenyl)phosphonium, tri(dimethylphenyl)phosphonium, dimethylsulphonium, diethylsulphonium, and diphenylsulphonium.

10 A second type of suitable cations corresponds to the formula:



wherein \textcircled{C}^{+} is a stable carbonium or silylium ion containing up to 30 nonhydrogen atoms, the cation being capable of reacting with a substituent of the transition metal compound and converting it into a

15 catalytically active transition metal complex, especially a cationic transition metal complex. Suitable examples of cations include tropylium, triphenylmethylium, benzene(diazonium). Silylium salts have been previously generically disclosed in J. Chem. Soc. Chem. Comm., 1993, pp. 383-384, as well as Lambert, J.B., et. al., Organometallics, 1994, 13,

20 pp. 2430-2443. Preferred silylium cations are triethylsilylium, and trimethylsilylium and ether substituted adducts thereof.

Another suitable type of cation comprises a cationic oxidizing agent represented by the formula:



25 wherein Ox^{e+} is a cationic oxidizing agent having a charge of e^{+} , and e is an integer from 1 to 3.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^{+} , and Pb^{2+} .

The quantity of activator compound in the supported catalyst

30 component and the supported catalyst is not critical, but typically ranges from 0.1, preferably from 1 to 2,000 micromoles of activator compound per gram of treated support material. Preferably, the supported catalyst or

component contains from 10 to 1,000 micromoles of activator compound per gram of treated support material.

Generally, the ratio of moles of activator compound to gramatoms of transition metal in the supported catalyst is from 0.05:1 to 100:1, preferably from 0.5:1 to 20:1 and most preferably from 1:1 to 5:1 mole activator compound per gramatom of transition metal in the supported catalyst. At too low ratios the supported catalyst will not be very active, whereas at too high ratios the catalyst becomes less economic due to the relatively high cost associated with the use of large quantities of activator compound.

The supported catalyst according to this embodiment can be prepared by combining the support material with the organometal compound and the activator compound. The order of addition is not critical. The organometal compound may be either first combined with the support material or with the activator compound, and subsequently the activator compound or the support material may be added. One preferred embodiment comprises treating the support material first with the organometal compound by combining the organometal compound in a suitable solvent, such as a hydrocarbon solvent, with the support material. The temperature, pressure, and contact time for this treatment are not critical, but generally vary from -20°C to about 150°C, from subatmospheric to 10 bar, more preferably at atmospheric pressure, for 5 minutes to 48 hours. Usually the slurry is agitated. After this treatment the solids are typically separated from the solvent. Any excess of organometal compound could then be removed by techniques known in the art. This method is especially suitable for obtaining support material with relatively low metal loadings.

According to a preferred embodiment, the support material is first subjected to a thermal treatment at 100°C to 1000°C, preferably at 200°C to 850°C. Typically, this treatment is carried out for 10 minutes to 72 hours, preferably from 0.5 hours to 24 hours. Then the thermally treated support material is combined with the organometal compound, preferably AlR'_3 wherein R' has the meaning defined hereinbefore in a suitable diluent or solvent, preferably one in which the organometal compound is soluble. Typical solvents are hydrocarbon solvents having from 5 to 12 carbon atoms, preferably aromatic solvents such as toluene and xylenes, or

aliphatic solvents of 6 to 10 carbon atoms, such as hexane, heptane, octane, nonane, decane, and isomers thereof, cycloaliphatic solvents of 6 to 12 carbon atoms such as cyclohexane, or mixtures of any of these.

5 The support material is combined with the organometal compound at a temperature of -20°C to 150°C, preferably at 20°C to 100°C. The contact time is not critical and can vary from 5 minutes to 72 hours, and is preferably from 0.5 hours to 36 hours. Agitation is preferably applied. The thus treated support material is then preferably contacted with the activator compound.

10 An alternative treatment of the support material, suitable for obtaining alumoxane loadings attached to the support material, involves one or both of the following steps (A) and (B):

(A) heating a support material containing alumoxane under an inert atmosphere for a period and at a temperature sufficient to fix alumoxane to the support material;

(B) subjecting the support material containing alumoxane to one or more wash steps to remove alumoxane not fixed to the support material;

thereby selecting the conditions in heating step A and washing step B so as to form a treated support material wherein not more than 10 percent aluminum present in the treated support material is extractable in a one hour extraction with toluene of 90°C using about 10 mL toluene per gram of supported catalyst component. High amounts of alumoxane attached to the support material are obtained using first heating step A, optionally followed by wash step B.

25 In this process the alumoxane treated support material may be obtained by combining in a diluent an alumoxane with a support material containing from zero to not more than 20 weight percent of water, preferably from zero to not more than 6 weight percent of water, based on the total weight of support material and water. The alumoxane desirably is used in a dissolved form.

Alternatively, the alumoxane pretreated support material may be obtained by combining in a diluent, a support material containing from 0.5 to 50 weight percent water, preferably from 1 to 20 weight percent water, based on the total weight of support material and water, with a compound

of the formula $R_n \cdot AlX_{3-n}$ wherein R" in independently each occurrence is a hydrocarbyl radical, X" is halogen or hydrocarbyloxy, and n* is an integer from 1 to 3. Preferably, n* is 3. R" in independently each occurrence is preferably an alkyl radical, advantageously one containing
5 from 1 to 12 carbon atoms. Preferred alkyl radicals are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, iso-pentyl, hexyl, iso-hexyl, heptyl, octyl, and cyclohexyl. Highly preferred compounds of formula $R_n \cdot AlX_{3-n}$ are trimethylaluminum, triethylaluminum and tri-isobutylaluminum. When the alumoxane is prepared *in situ* by
10 reacting the compound of the formula $R_n \cdot AlX_{3-n}$ with water, the mole ratio of $R_n \cdot AlX_{3-n}$ to water is typically 10:1 to 1:1, preferably from 5:1 to 1:1.

The support material is added to the alumoxane or compound of the formula $R_n \cdot AlX_{3-n}$, preferably dissolved in a solvent, most preferably a
15 hydrocarbon solvent, or the solution of alumoxane or compound of the formula $R_n \cdot AlX_{3-n}$ is added to the support material. The support material can be used as such in dry form or slurried in a hydrocarbon diluent. Both aliphatic and aromatic hydrocarbons can be used. Suitable aliphatic hydrocarbons include, for example, pentane, isobutane
20 isopentane, hexane, heptane, octane, iso-octane, nonane, isononane, decane, cyclohexane, methylcyclohexane and combinations of two or more of such diluents. Examples of suitable aromatic diluents are benzene, toluene, xylene, and other alkyl or halogen-substituted aromatic compounds. Most preferably, the diluent is branched paraffin such as, for
25 example, an aromatic hydrocarbon, especially toluene. Suitable concentrations of solid support in the hydrocarbon medium range from 0.1 to 15, preferably from 0.5 to 10, more preferably from 1 to 7 weight percent. The contact time and temperature are not critical. Preferably the temperature is from 0°C to 60°C, more preferably from 10°C to 40°C.
30 The contact time is from 15 minutes to 40 hours, preferably from 1 to 20 hours.

Before subjecting the alumoxane-treated support material to the heating step or washing step, the diluent or solvent is preferably removed to obtain a free flowing powder. This is preferably done by applying a
35 technique which only removes the liquid and leaves the aluminum compounds on the solids, such as by applying heat, reduced pressure, evaporation, or

a combination thereof. If desired, the removal of diluent can be combined with the heating step, although care should be taken that the diluent is removed gradually.

The heating step and the washing step are conducted in such a way that a very large proportion (more than 90 percent by weight) of the alumoxane which remains on the support material is fixed. Preferably, a heating step is used, more preferably a heating step is used followed by a washing step. When used in the preferred combination both steps cooperate such that in the heating step the alumoxane is fixed to the support material, whereas in the washing step the alumoxane which is not fixed is removed to a substantial degree. The upper temperature for the heat-treatment is preferably below the temperature at which the support material begins to agglomerate and form lumps which are difficult to redisperse, and below the alumoxane decomposition temperature. When the transition metal compound c) is added before the heat treatment, the heating temperature should be below the decomposition temperature of the transition metal compound. Preferably, the heat-treatment is carried out at a temperature from 75°C to 250°C for a period from 15 minutes to 24 hours. More preferably, the heat treatment is carried out at a temperature from 160°C to 200°C for a period from 30 minutes to 4 hours. Good results have been obtained while heating for 8 hours at 100°C as well as while heating for 2 hours at 175°C. By means of preliminary experiments, a person skilled in the art will be able to define the heat-treatment conditions that will provide the desired result. It is also noted, that the longer the heat treatment takes, the higher the amount of alumoxane fixed to the support material will be. The heat-treatment is carried out at reduced pressure or under an inert atmosphere, such as nitrogen gas, or both but preferably at reduced pressure. Depending on the conditions in the heating step, the alumoxane may be fixed to the support material to such a high degree that a wash step may be omitted.

In the wash step, the number of washes and the solvent used are such that sufficient amounts of non-fixed alumoxane are removed. The washing conditions should be such that non-fixed alumoxane is soluble in the wash solvent. The support material containing alumoxane, preferably already subjected to a heat-treatment, is preferably subjected to one to five wash steps using an aromatic hydrocarbon solvent at a temperature from 0°C to 110°C. More preferably, the temperature is from 20°C to 100°C. Examples

of suitable aromatic solvents include toluene, benzene and xylenes. More preferably, the aromatic hydrocarbon solvent is toluene. At the end of the wash treatment, the solvent is removed by a technique that also removes the alumoxane dissolved in the solvent, such as by filtration or
5 decantation. Preferably, the wash solvent is removed to provide a free flowing powder.

The organometal compound treated support material is then typically reslurried in a suitable diluent and combined with the activator compound. The activator compound is preferably used in a diluent. Suitable diluents
10 include hydrocarbon and halogenated hydrocarbon diluents. Any type of solvent or diluent can be used which does not react with the catalyst components in such a way as to negatively impact the catalytic properties. Preferred diluents are aromatic hydrocarbons, such as toluene, benzene, and xylenes, and aliphatic hydrocarbons such as hexane, heptane, and
15 cyclohexane. Preferred halogenated hydrocarbons include methylene chloride and carbon tetrachloride. The temperature is not critical but generally varies between -20°C and the decomposition temperature of the activator. Typical contact times vary from a few minutes to several days. Agitation of the reaction mixture is preferred. Advantageously, the
20 activator compound is dissolved, using heat to assist in dissolution where desired. It may be desirable to carry out the contacting between the organometal-treated support material and the activator compound at elevated temperatures. Preferably, such elevated temperatures are from 45°C to 120°C.

25 Instead of first treating the support material with the organometal compound, preferably aluminum component, and subsequently adding the activator compound, the organometal compound, preferably aluminum component, and activator compound may be combined in a suitable diluent prior to adding or combining the reaction mixture to or with the thermally
30 treated support material or the support material containing from 0.5 to 50 weight percent water.

Without wishing to be bound by any theory, it is believed that an organo group of the organometal compound reacts with the active hydrogen moiety contained in the activator anion (b-2) to form a reaction or
35 contact product (hereinafter also referred to as "adduct"). For example, when the organometal compound is trialkylaluminum AlR_3 and the active

hydrogen-containing moiety is represented by G-OH, the reaction product is believed to comprise G-O-AlR₂ whereas further an alkane by-product RH is formed. This adduct G-O-AlR₂ when combined with the support material containing hydroxyl groups, Si-OH in case of a silica support material, is
5 believed to form Si-O-Al(R)-O-G together with alkane RH as by-product. This method of preparing the supported catalyst component has been found to run very smoothly and to provide catalysts and catalyst precursors or components having desirable properties. Typical ratios to be used in this reaction are from 1:1 to 20:1 moles of organometal compound to mole
10 equivalents of active hydrogen moieties contained in the activator anion (b-2).

The amount of adduct, formed by combining the organometal compound with the activator compound, to be combined with the support material is not critical. Preferably, the amount is not higher than can be fixed to
15 the support material. Typically, this is determined by the amount of support material hydroxyls. The amount of adduct to be employed is preferably not more than the equivalent amount of such hydroxyl groups. Less than the equivalent amount is preferably used, more preferably the ratio between moles of adduct to moles of surface reactive groups such as
20 hydroxyls is between 0.01 and 1, even more preferably between 0.02 and 0.8. Prior to adding the transition metal compound it is preferred, especially when less than an equivalent amount of adduct is added with respect to surface reactive groups, to add an additional amount of organometal compound to the reaction product of support material and the
25 adduct to remove any remaining surface reactive groups which otherwise may react with the transition metal and thus require higher amounts thereof to achieve equal catalytic activity. Prior to combining it with the transition metal compound, the supported catalyst component can be washed, if desired, to remove any excess of adduct or organometal
30 compound.

The supported catalyst component comprising the support material, organometal compound, and the activator may be isolated to obtain a free flowing powder by removing the liquid medium using preferably filtration or evaporation techniques.

35 Although the transition metal compound may be combined with the activator compound, or the adduct of the organometal compound and the

activator compound, prior to combining the activator compound or its adduct with the support material, this results in reduced catalyst efficiencies. Preferably, the transition metal is first combined with the support material treated with the organometal component and before adding
5 the activator compound, or the transition metal is added after the treated support material and activator have been combined, or after the activator adduct and the support material have been combined. Most preferably, the transition metal compound (c) is added to the reaction product of the support material treated with the organometal compound and activator
10 compound, or after the activator adduct and the support material have been combined.

The transition metal compound is preferably used dissolved in a suitable solvent, such as a hydrocarbon solvent, advantageously a C₅-C₁₀ aliphatic or cycloaliphatic hydrocarbon or a C₆-C₁₀ aromatic hydrocarbon.
15 The contact temperature is not critical provided it is below the decomposition temperature of the transition metal and of the activator. Good results are obtained in a temperature range of 0°C to 100°C. All steps in the present process should be conducted in the absence of oxygen and moisture.

20 Upon combining the transition metal compound with the supported catalyst component, the supernatant liquid typically is colorless indicating that the transition metal compound, which solution typically is colored, substantially remains with the solid supported catalyst.

According to an alternative preferred embodiment the solid (or
25 supported) catalyst comprises:

a supported catalyst component comprising a support material and an alumoxane wherein not more than 10 percent aluminum present in the supported catalyst component is extractable in a one hour extraction with toluene of 90°C using 10 ml toluene per gram of supported catalyst
30 component;

and a transition metal compound.

This solid catalyst according to this embodiment may be used in the absence of the activator compound comprising (b-1) a cation which is capable of reacting with a transition metal compound to form a

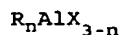
catalytically active transition metal complex, and (b-2) a compatible anion having up to 100 nonhydrogen atoms and containing at least one substituent comprising an active hydrogen moiety.

According to this alternative embodiment, the aluminum atom (from the alumoxane component) to transition metal atom mole ratio in the supported catalyst generally is from 1 to 5000, preferably from 25 to 1000 and most preferably from 50 to 500.

The quantity of transition metal compound in the supported catalyst of the present invention is not critical, but typically ranges from 0.1 to 1000 micromoles of transition metal compound per gram of support material. Preferably, the supported catalyst contains from 1 to 250 micromoles of transition metal compound per gram of support material.

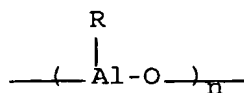
The supported catalyst according to this embodiment is obtainable by heating or washing a support material containing alumoxane under an inert atmosphere for a period and at a temperature sufficient to fix alumoxane to the support material, as discussed above.

It may be advantageous to use in the present process the solid catalyst in association with impurity scavengers which serve to protect the solid catalyst from catalyst poisons such as water, oxygen, and polar compounds. Preferred compounds for this purpose include an organoaluminum compound represented by the following formula:



wherein R is a C₁-C₂₀ hydrocarbyl group; X is a halogen atom or a C₁-C₂₀ hydrocarbyloxy group; and n is a positive integer selected from 1 to 3,

or an organoaluminumoxy compound represented by the following formula:



wherein R is a C₁-C₂₀ hydrocarbyl group; and n is a positive integer selected from 5 to 50.

By the treatment with the organoaluminum compound or the organoaluminumoxy compound, the resistance of the solid catalyst system to impurities, such as water, oxygen and the like which are present in the solid catalyst system, can be improved, and the solid catalyst system can be stored for a prolonged period of time.

In the above treatment, the organoaluminum compound or the organoaluminumoxy compound is used preferably in an amount of 0.1 to 100 mol in terms of aluminum, more preferably in an amount of 1 to 30 mol, per mol of a transition metal compound contained in the solid catalyst system. It is noted that the organoaluminumoxy compound should preferably not be used in amount that may cause desorption of the transition metal compound from the solid catalyst. The solid catalyst system to be used in the method of the present invention can be stored in the form of a slurry thereof in an inert hydrocarbon solvent, or dried and stored in a solid form thereof.

Suitable activating cocatalysts useful in combination with the single site catalyst component are those compounds capable of abstraction of an X substituent therefrom to form an inert, noninterfering counter ion, or that form a zwitterionic derivative of the catalyst component. Suitable activating cocatalysts for use herein include perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, and ferrocenium salts of compatible, noncoordinating anions. Suitable activating techniques include the use of bulk electrolysis. A combination of the foregoing activating cocatalysts and techniques may be employed as well. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes in the following references: European Patent EP-A-277,003, US-A-5,153,157, US-A-5,064,802, European Patents EP-A-468,651 and EP-A-520,732 (equivalent to U. S. Serial No. 07/876,268 filed May 1, 1992), and US-A-5,350,723.

More particularly, suitable ion forming compounds useful as cocatalysts comprise a cation which is a Brønsted acid capable of donating

a proton, and a compatible, noncoordinating anion, A^- . As used herein, the term "noncoordinating" means an anion or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived therefrom, or which is only weakly

5 coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

10 Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic,
 15 diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or
 20 metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general formula:

25 $(L^*-H)^+_{d-} (A)^{d-}$

wherein:

L^* is a neutral Lewis base;

$(L^*-H)^+$ is a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of $d-$,

30 and

d is an integer from 1 to 3.

More preferably A^{d-} corresponds to the formula: $[M'Q_d]^-$;

wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo-substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl-perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxy Q groups are disclosed in U. S. Patent 5,296,433.

In a more preferred example, d is one, that is, the counter ion has a single negative charge and is A⁻. Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

(L*-H)⁺(BQ₄)⁻;

wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst for the present invention are tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,

triethylammonium tetrakis(pentafluorophenyl) borate,

tripropylammonium tetrakis(pentafluorophenyl) borate,

- tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-dodecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-octadecylammonium tetrakis(pentafluorophenyl) borate,
5 N-methyl-N,N-didodecylammonium tetrakis(pentafluorophenyl) borate,
N-methyl-N,N-diocadecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
10 N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-2, 3, 5, 6-
tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-
tetrafluorophenyl) borate,
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
15 N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
20 tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate, and
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)
25 borate;

disubstituted ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and

dicyclohexylammonium tetrakis(pentafluorophenyl) borate;

trisubstituted phosphonium salts such as:

5 triphenylphosphonium tetrakis(pentafluorophenyl) borate,

tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and

tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;

disubstituted oxonium salts such as:

diphenyloxonium tetrakis(pentafluorophenyl) borate,

10 di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and

di(2,6-dimethylphenyl)oxonium tetrakis(pentafluorophenyl) borate;

disubstituted sulfonium salts such as:

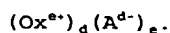
diphenylsulfonium tetrakis(pentafluorophenyl) borate,

di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and

15 bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate.

Preferred (L⁺-H)⁺ cations are N,N-dimethylanilinium, tributylammonium, N-methyl-N,N-didodecylammonium, N-methyl-N,N-dioctadecylammonium, and mixtures thereof.

Another suitable ion forming, activating cocatalyst comprises a salt
20 of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein Ox^{e+}, A^{d-} and d are as previously defined.

Examples of cationic oxidizing agents include: ferrocenium,
25 hydrocarbyl-substituted ferrocenium, Ag⁺ or Pb²⁺. Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted

acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

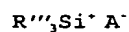
Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating,
5 compatible anion represented by the formula:



wherein:

R^+ and A^- are as previously defined. A preferred carbenium ion is the trityl cation, that is triphenylmethylium.

10 A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

15 R''' is C_{1-10} hydrocarbyl, and A^- are as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether substituted adducts thereof. The use of the above silylium salts as activating cocatalysts for addition
20 polymerization catalysts is claimed in USSN 08/304,314, filed September 12, 1994.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used for the present invention. Such cocatalysts are disclosed in
25 USP 5,296,433.

The most preferred activating cocatalysts are trispentafluorophenylborane and N,N-diocetadecyl-N-methylammonium tetrakis(pentafluorophenyl)borate. The latter compound being the principal component of a mixture of borate salts derived from bis(hydrogenated
30 tallow)methylammonium compounds, which mixture may be used as the activating cocatalyst herein.

The molar ratio of metal complex: activating cocatalyst employed preferably ranges from 1:10 to 2:1, more preferably from 1:5 to 1.5:1, most preferably from 1:5 to 1:1.

Other activators include the previously described aluminoxanes. Preferred aluminoxanes include methylaluminoxane, propylaluminoxane, isobutylaluminoxane, combinations thereof and the like. So-called modified methylaluminoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified alumoxane is disclosed in U.S. Patent No. 4,960,878 (Crapo et al.). Aluminoxanes can also be made as disclosed in U.S. patents Nos. 4,544,762 (Kaminsky et al.); 5,015,749 (Schmidt et al.); 5,041,583 (Sangokoya); 5,041,584 (Crapo et al.); and 5,041,585 (Deavenport et al.). When aluminoxanes are used as the activating cocatalyst, the molar ratio of transition metal complex: aluminum preferably ranges from 1:2,000 to 2:1, more preferably from 1:1,000 to 1.5:1, most preferably from 1:500 to 1:1.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0-250 °C, preferably 30 to 200 °C and pressures from atmospheric to 30,000 atmospheres or higher. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A solid component (other than that used to prepare the catalysts used to make the ethylene homopolymer of the present invention), may be employed especially silica, alumina, or a polymer (especially poly(tetrafluoroethylene) or a polyolefin), and desirably is employed when the catalysts are used in a gas phase polymerization process. The support is preferably employed in an amount to provide a weight ratio of catalyst (based on metal):support from 1:100,000 to 1:10, more preferably from 1:50,000 to 1:20, and most preferably from 1:10,000 to 1:30.

In most polymerization reactions the molar ratio of catalyst:polymerizable compounds employed is from 10^{-12} :1 to 10^{-1} :1, more preferably from 10^{-9} :1 to 10^{-5} :1.

Suitable solvents for polymerization are inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and

alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C₄₋₁₀ alkanes, and the like and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, ethylbenzene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-heptene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), and the like. Mixtures of the foregoing are also suitable.

The polymerization conditions for manufacturing the higher density ethylene homopolymer of the present invention are generally those useful in the slurry polymerization process provided the proper catalysts and polymerization conditions are employed. A description of the slurry process can be found in Volume 6 of the Encyclopedia of Polymer Science and Engineering, (John Wiley and Sons) pages 472 to 477.

By conducting the slurry polymerization under appropriately controlled reaction conditions, the ethylene copolymer being formed around the solid catalyst system is not melted or dissolved during the polymerization reaction, but maintains a powdery form (which powdery form is achieved by the use of the above-mentioned specific catalyst system) during the reaction.

The polymerization reaction to produce the inventive ethylene polymer is conducted under slurry process conditions at ethylene conversion rates of greater than 92 percent, preferably greater than or equal to 95 percent, more preferably greater than or equal to 98 percent, per pass; preferably at polymerization pressures generally from 1 to 100 atm, preferably from 3 to 30 atm, and preferably at polymerization temperatures generally from greater than 50°C, especially greater than or equal to 60°C, more especially greater than or equal to 70°C, most especially in the range of from 70°C to 110°C. But the upper limit of the polymerization temperature is a temperature which is the highest temperatures at which the ethylene interpolymer produced can be maintained in substantially a powdery state. This temperature varies depending on the density of the ethylene polymer being produced and the type of diluent.

used.

As a suitable diluent, inert aliphatic hydrocarbon solvents are employed. Preferably, a high temperature diluent such as a branched paraffin (or mixtures therewith) is used, for example, isopentane, isobutane, dimethylpropane, dimethylenebutane or dimethylpentane, more preferably isobutane or dimethylpropane, most preferably isobutane, which mitigates against agglomeration of polymer particles being formed during the polymerization.

In producing the higher density ethylene homopolymer, the molecular weight can be controlled by changing the content of hydrogen in the reaction system or by changing the polymerization temperature, as described in DE 3127133.2.

In the present invention, the solid catalyst system may contain, in addition to the above-mentioned components, various additives which are known to be useful for ethylene polymerization.

The ethylene homopolymers of the present invention have the following unusual combination of properties.

The density satisfies the following inequality;

$$\text{density (g/cm}^3\text{)} > 0.9611 + 0.0058 \log (I_2) - 0.00128 \log^2 (I_2)$$

In addition the density is of from 0.915 to 0.985, preferably of from 0.935 to 0.983, more preferably of from 0.945 to 0.980 g/cm³.

The melt index (I_2) is of from 0.0001 to 10,000, preferably of from 0.001 to 5,000, more preferably of from 0.01 to 3,000 g/10 min.

The I_{21}/I_2 ratio is of from 15 to 65, preferably of from 18 to 55, more preferably of from 20 to 50, or the I_{10}/I_2 ratio is of from 5 to 30, preferably of from 5 to 28, more preferably of from 5.5 to 25.

The M_w/M_n ratio (as measured by GPC) greater than 2.5, preferably from 2.5 to 10, more preferably from 2.8 to 8, most preferably from 3 to 6.

Preferably, the inventive ethylene homopolymer is further characterized as having a M_w/M_n ratio which satisfies the following inequalities:

$$M_w/M_n \geq 22.8 - 3.3 \log M_w; \text{ especially}$$

5 $M_w/M_n \geq 33.1 - 4.78 \log M_w; \text{ more especially}$

$$M_w/M_n \geq 45.6 - 6.6 \log M_w; \text{ even more especially}$$

$$3.1 - 0.15 \log M_w - 2.5 \geq M_w/M_n \geq 22.8 - 3.3 \log M_w$$

In addition to the ethylene homopolymer, also included in the current invention are blend compositions comprising the ethylene
10 homopolymer (Component A) with various other ethylene interpolymers or homopolymers (Component B).

Blends of the ethylene homopolymer with homogeneous narrow composition interpolymers, most preferably the substantially linear ethylene/ α -olefin interpolymers are another aspect of the present
15 invention. The homogeneous polymers and interpolymers components of the blend compositions are herein defined as defined in USP 3,645,992 (Elston). Accordingly, homogeneous polymers and interpolymers are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have
20 the same ethylene/comonomer ratio within that interpolymer. Such interpolymers are distinct from the typical Ziegler catalyzed interpolymers which are known as heterogeneous interpolymers and are those in which the interpolymer molecules do not have the same ethylene/comonomer ratio. The homogeneous polymers are also distinct from
25 LDPE produced by high pressure free radical catalyzed ethylene polymerization which results in highly branched polyethylene which is known to those skilled in the art to have numerous long chain branches.

The term "narrow composition distribution" used herein describes the comonomer distribution for homogeneous interpolymers and means that the
30 homogeneous interpolymers have only a single melting peak as measured by Differential Scanning Calorimetry (DSC) and essentially lack a measurable "linear" polymer fraction.

The narrow composition distribution homogeneous interpolymers can also be characterized by their SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) which is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Patent 4,798,081 (Hazlitt et al.), or as is described in USP 5,008,204 (Stehling). The technique for calculating CDBI is described in USP 5,322,728 (Davey et al.) and in USP 5,246,783 (Spenadel et al.) or in U.S. Patent 5,089,321 (Chum et al.). The SCBDI or CDBI for the homogeneous narrow composition ethylene/ α -olefin interpolymers used in the present invention is preferably greater than 50 percent, especially greater than 70 percent, most preferably greater than 90 percent.

The narrow composition distribution homogeneous interpolymer blend components of this invention essentially lack a measurable "high density" (or homopolymer) fraction as measured by the TREF technique. The homogeneous interpolymers and polymers have a degree of branching less than or equal to 2 methyls/1000 carbons in 15 percent (by weight) or less, preferably less than 10 percent (by weight), and especially less than 5 percent (by weight).

Preferred components of the blends of the current invention are the substantially linear ethylene/ α -olefin interpolymers. The substantially linear ethylene/ α -olefin interpolymers are herein defined as in US Pat. Nos. 5,272,236 and 5,278,272. The substantially linear ethylene/ α -olefin interpolymers are also homogeneous interpolymers as the comonomer is randomly distributed within a given interpolymer molecule and substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer.

However the term "substantially linear" ethylene/ α -olefin interpolymer means that the polymer also contains long chain branching. More specifically, the polymer backbone of a substantially linear ethylene/ α -olefin interpolymer is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more

preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons.

5 The substantially linear ethylene/ α -olefin interpolymers useful in this invention surprisingly have excellent processability, even though they have relatively narrow molecular weight distributions. The substantially linear ethylene/ α -olefin interpolymers have a molecular weight distribution, M_w/M_n , defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63.$$

10 Even more surprising, the melt flow ratio (I_{10}/I_2) of the substantially linear olefin polymers can be varied essentially independently of the polydispersity index (that is, molecular weight distribution (M_w/M_n)). This is contrasted with conventional heterogeneously branched linear polyethylene resins having rheological
15 properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

For the substantially linear ethylene/ α -olefin polymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, that is, the higher the I_{10}/I_2 ratio, the more long
20 chain branching in the polymer.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, no. 11, p. 770 (1977), and
25 in Rheometers for Molten Plastics by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97-99. All GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene/ α -olefin polymers described herein, the
30 PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/cm². The substantially linear ethylene/ α -olefin interpolymers described herein preferably have a PI in the range of 0.01 kpoise to 50 kpoise, preferably 15 kpoise or less. The substantially linear ethylene/ α -olefin polymers described herein have a PI

less than or equal to 70 percent of the PI of a comparative linear ethylene/ α -olefin polymer which does not contain long chain branching but of about the same I_2 and M_w/M_n .

5 An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

10 Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The critical shear rate at onset of surface melt fracture
15 for the substantially linear ethylene/ α -olefin interpolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene/ α -olefin polymer which does not contain long chain branching but of about the same I_2 and M_w/M_n , wherein "about the same" as used herein means that each value is within 10 percent of the
20 comparative value of the comparative linear ethylene polymer.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown film products), surface defects should be minimal, if not absent. The
25 critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

The homogeneous interpolymer component of the blend can be an ethylene homopolymer or, preferably, interpolymers of ethylene with at
30 least one comonomer selected from the group consisting of a compound represented by the formula $H_2C=CHR$ wherein R is a C_1-C_{18} linear, branched or cyclic alkyl group or a C_6-C_{20} aryl group, and a C_4-C_{20} linear, branched or cyclic diene. Illustrative examples of the compounds represented by the formula $H_2C=CHR$ include propylene, 1-butene, 1-pentene, 1-hexene, 4-
35 methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-

tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexene and styrene. Illustrative examples of C_4 - C_{20} linear, branched and cyclic dienes include 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene and cyclo hexadiene. Of these, propylene, 1-butene, 1-pentene, 1-hexene, 5 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene are especially preferred.

The homogeneous narrow composition distribution ethylene/ α -olefin interpolymer component may be prepared using the previously described 10 single site catalysts. Preparation of the homogeneous narrow composition distribution substantially linear ethylene/ α -olefin polymers requires the use of the previously described constrained geometry single site catalysts.

Blends of the ethylene homopolymers can also be prepared with 15 heterogeneous broad composition distribution ethylene interpolymers. The heterogeneous component is differentiated from the homogeneous component in that in the latter, substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer, whereas heterogeneous interpolymers are those in which the interpolymer molecules 20 do not have the same ethylene/comonomer ratio. The term "broad composition distribution" used herein describes the comonomer distribution for heterogeneous interpolymers and means that the heterogeneous interpolymers have a "linear" fraction and that the heterogeneous interpolymers have multiple melting peaks (that is, exhibit at least two 25 distinct melting peaks) by DSC. In 10 percent (by weight) or more, preferably more than 15 percent (by weight), and especially more than 20 percent (by weight, the heterogeneous interpolymers and polymers have a degree of branching less than or equal to 2 methyls/1000 carbons. Also, in 25 percent or less (by weight), preferably less than 15 percent (by 30 weight), and especially less than 10 percent (by weight), the heterogeneous interpolymers have a degree of branching equal to or greater than 25 methyls/1000 carbons.

The heterogeneous interpolymer component of the blend can also be an ethylene homopolymer or, preferably, interpolymers of ethylene with at 35 least one comonomer selected from the group consisting of a compound represented by the formula $H_2C=CHR$ wherein R is a C_1 - C_{18} linear, branched

or cyclic alkyl group or a C₆-C₂₀ aryl group, and a C₄-C₂₀ linear, branched or cyclic diene. Illustrative examples of the compounds represented by the formula H₂C=CHR include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexene and styrene. Illustrative examples of C₄-C₂₀ linear, branched and cyclic dienes include 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene and cyclo hexadiene. Of these, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene are especially preferred. Heterogeneous interpolymers of ethylene and 1-butene, 1-pentene, 1-hexene, 1-heptene, or 1-octene are most preferred.

Ziegler-Natta catalysts may be used to prepare the heterogeneous component of the polymer blend. Preferred Ziegler-Natta catalysts include magnesium alkoxide-based catalysts, such as those taught by USP 4,526,943, USP 4,426,316, 4,661,465, USP 4,783,512, and USP 4,544,647. Such catalysts are particularly useful if the heterogeneous polymer component is to be prepared under slurry process conditions.

Additional examples of Ziegler-type catalysts which are particularly useful if the heterogeneous polymer blend component is to be prepared under the high polymerization temperatures of the solution process, include catalysts derived from organomagnesium compounds, alkyl halides or aluminum halides or hydrogen chloride, and a transition metal compound. Examples of such catalysts are described in U.S. Pat Nos. 4,314,912 (Lowery, Jr. et al.), 4,547,475 (Glass et al.), and 4,612,300 (Coleman, III).

Particularly suitable organomagnesium compounds include, for example, hydrocarbon soluble dihydrocarbylmagnesium such as the magnesium dialkyls and the magnesium diaryls. Exemplary suitable magnesium dialkyls include particularly n-butyl-sec-butylmagnesium, diisopropylmagnesium, di-n-hexylmagnesium, isopropyl-n-butyl-magnesium, ethyl-n-hexylmagnesium, ethyl-n-butylmagnesium, di-n-octylmagnesium and others wherein the alkyl has from 1 to 20 carbon atoms. Exemplary suitable magnesium diaryls include diphenylmagnesium, dibenzylmagnesium and ditolylmagnesium. Suitable organomagnesium compounds include alkyl and aryl magnesium

alkoxides and aryloxides and aryl and alkyl magnesium halides with the halogen-free organomagnesium compounds being more desirable.

Among the halide sources which can be employed herein are the active non-metallic halides, metallic halides, and hydrogen chloride. Suitable non-metallic halides are represented by the formula $R'X$ wherein R' is hydrogen or an active monovalent organic radical and X is a halogen. Particularly suitable non-metallic halides include, for example, hydrogen halides and active organic halides such as *t*-alkyl halides, allyl halides, benzyl halides and other active hydrocarbyl halides wherein hydrocarbyl is as defined hereinbefore. By an active organic halide is meant a hydrocarbyl halide that contains a labile halogen at least as active, that is, as easily lost to another compound, as the halogen of *sec*-butyl chloride, preferably as active as *t*-butyl chloride. In addition to the organic monohalides, it is understood that organic dihalides, trihalides and other polyhalides that are active as defined herein before are also suitably employed. Examples of preferred active non-metallic halides include hydrogen chloride, hydrogen bromide, *t*-butyl chloride, *t*-amyl bromide, allyl chloride, benzyl chloride, crotyl chloride, methylvinyl carbonyl chloride, α -phenylethyl bromide, diphenyl methyl chloride and the like. Most preferred are hydrogen chloride, *t*-butyl chloride, allyl chloride and benzyl chloride.

Suitable metallic halides which can be employed herein include those represented by the formula MR_y-aX_a wherein:

M is a metal of Groups IIB, IIIA or IVA of Mendeleev's Periodic Table of Elements,

R is a monovalent organic radical,

X is a halogen,

Y has a value corresponding to the valence of M , and a has a value from 1 to y .

Preferred metallic halides are aluminum halides of the formula AlR_3-aX_a wherein:

each R is independently hydrocarbyl as hereinbefore defined such as alkyl.

X is a halogen; and

a is a number from 1 to 3.

Most preferred are alkylaluminum halides such as ethylaluminum sesquichloride, diethylaluminum chloride, ethylaluminum dichloride, and
5 diethylaluminum bromide, with ethylaluminum dichloride being especially preferred. Alternatively, a metal halide such as aluminum trichloride or a combination of aluminum trichloride with an alkyl aluminum halide or a trialkyl aluminum compound may be suitably employed.

It is understood that the organic moieties of the aforementioned
10 organomagnesium, for example, R", and the organic moieties of the halide source, for example, R and R', are suitably any other organic radical provided that they do not contain functional groups that poison conventional Ziegler catalysts.

The magnesium halide can be preformed from the organomagnesium
15 compound and the halide source or it can be formed in situ in which instance the catalyst is preferably prepared by mixing in a suitable solvent or reaction medium (1) the organomagnesium component and (2) the halide source, followed by the other catalyst components.

Any of the conventional Ziegler-Natta transition metal compounds can
20 be usefully employed as the transition metal component in preparing the supported catalyst component. Typically, the transition metal component is a compound of a Group IVB, VB, or VIB metal. The transition metal component is generally, represented by the formulas: $\text{TrX}'_{4-q}(\text{OR}^1)_q$, $\text{TrX}'_{4-q}\text{R}^2_q$, VOX'_3 and $\text{VO}(\text{OR}^1)_3$.

25 Tr is a Group IVB, VB, or VIB metal, preferably a Group IVB or VB metal, preferably titanium, vanadium or zirconium,

q is 0 or a number equal to or less than 4,

X' is a halogen, and

R¹ is an alkyl group, aryl group or cycloalkyl group having from 1
30 to 20 carbon atoms, and

R² is an alkyl group, aryl group, aralkyl group, substituted aralkyls, and the like. The aryl, aralkyls and substituted aralkyls

contain 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms. When the transition metal compound contains a hydrocarbyl group, R^2 , being an alkyl, cycloalkyl, aryl, or aralkyl group, the hydrocarbyl group will preferably not contain an H atom in the position beta to the metal carbon

5 bond. Illustrative but non-limiting examples of aralkyl groups are methyl, neo-pentyl, 2,2-dimethylbutyl, 2,2-dimethylhexyl; aryl groups such as benzyl; cycloalkyl groups such as 1-norbornyl. Mixtures of these transition metal compounds can be employed if desired.

Illustrative examples of the transition metal compounds include

10 $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)_3Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_8H_{17})_2Br_2$, and $Ti(OC_{12}H_{25})Cl_3$, $Ti(O-i-C_3H_7)_4$, and $Ti(O-n-C_4H_9)_4$.

Illustrative examples of vanadium compounds include VCl_4 , $VOCl_3$, $VO(OC_2H_5)_3$, and $VO(OC_4H_9)_3$.

15 Illustrative examples of zirconium compounds include $ZrCl_4$, $ZrCl_3(OC_2H_5)$, $ZrCl_2(OC_2H_5)_2$, $ZrCl(OC_2H_5)_3$, $Zr(OC_2H_5)_4$, $ZrCl_3(OC_4H_9)$, $ZrCl_2(OC_4H_9)_2$, and $ZrCl(OC_4H_9)_3$.

As indicated above, mixtures of the transition metal compounds may be usefully employed, no restriction being imposed on the number of

20 transition metal compounds which may be contracted with the support. Any halogenide and alkoxide transition metal compound or mixtures thereof can be usefully employed. The previously named transition metal compounds are especially preferred with vanadium tetrachloride, vanadium oxychloride, titanium tetraisopropoxide, titanium tetrabutoxide, and titanium

25 tetrachloride being most preferred.

Suitable catalyst materials may also be derived from a inert oxide supports and transition metal compounds. Examples of such compositions suitable for use in the solution polymerization process are described in U.S. Pat Nos. 5,420,090 (Spencer. et al.).

30 The inorganic oxide support used in the preparation of the catalyst may be any particulate oxide or mixed oxide as previously described which has been thermally or chemically dehydrated such that it is substantially free of adsorbed moisture.

The specific particle size, surface area, pore volume, and number of surface hydroxyl groups characteristic of the inorganic oxide are not critical to its utility in the practice of the invention. However, since such characteristics determine the amount of inorganic oxide to be employed in preparing the catalyst compositions, as well as affecting the properties of polymers formed with the aid of the catalyst compositions, these characteristics must frequently be taken into consideration in choosing an inorganic oxide for use in a particular aspect of the invention. In general, optimum results are usually obtained by the use of inorganic oxides having an average particle size in the range of 1 to 100 microns, preferably 2 to 20 microns; a surface area of 50 to 1,000 square meters per gram, preferably 100 to 400 square meters per gram; and a pore volume of 0.5 to 3.5 cm³ per gram; preferably 0.5 to 2 cm³ per gram.

In order to further improve catalyst performance, surface modification of the support material may be desired. Surface modification is accomplished by specifically treating the support material such as silica, alumina or silica-alumina with an organometallic compound having hydrolytic character. More particularly, the surface modifying agents for the support materials comprise the organometallic compounds of the metals of Group IIA and IIIA of the Periodic Table. Most preferably the organometallic compounds are selected from magnesium and aluminum organometallics and especially from magnesium and aluminum alkyls or mixtures thereof represented by the formulas and R^1MgR^2 and $R^1R^2AlR^3$ wherein each of R^1 , R^2 and R^3 which may be the same or different are alkyl groups, aryl groups, cycloalkyl groups, aralkyl groups, alkoxide groups, alkadienyl groups or alkenyl groups. The hydrocarbon groups R^1 , R^2 and R^3 can contain between 1 and 20 carbon atoms and preferably from 1 to 10 carbon atoms.

The surface modifying action is effected by adding the organometallic compound in a suitable solvent to a slurry of the support material. Contact of the organometallic compound in a suitable solvent and the support is maintained from 30 to 180 minutes and preferably from 60 to 90 minutes at a temperature in the range of 20° to 100° C. The diluent employed in slurrying the support can be any of the solvents

employed in solubilizing the organometallic compound and is preferably the same.

Blends of the inventive ethylene homopolymer can also be prepared with the inventive ethylene inventive polymer which is characterized as
5 having a molecular weight maximum occurring in that part of the composition that has the highest comonomer content.

The inventive interpolymer which has a molecular weight maximum occurring in the fraction having the highest comonomer content are prepared by interpolymerizing ethylene with at least one comonomer, under
10 slurry polymerization conditions in the presence of the previously described constrained geometry catalysts and the solid component used to prepare the ethylene homopolymers of the present invention. The interpolymerization reaction is conducted by slurry polymerization using the conditions defined herein above.

15 It is also important that the interpolymerization reaction is performed at a diffusion-limited rate. This means that the ethylene interpolymer produced must maintain a powdery state during the polymerization reaction. Therefore, the upper limit of the polymerization temperature is extremely important and must remain below the melting point
20 of the interpolymer.

Also ethylene is interpolymerized with at least one comonomer selected from the group consisting of a compound represented by the formula $H_2C=CHR$ wherein R is a C_1 - C_{18} linear, branched or cyclic alkyl group or a C_6 - C_{20} aryl group, and a C_4 - C_{20} linear, branched or cyclic
25 diene. Illustrative examples of the compounds represented by the formula $H_2C = CHR$ include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexene and styrene. Illustrative examples of C_4 - C_{20} linear, branched and cyclic dienes include
30 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene and cyclohexadiene. Of these, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene are especially preferred.

The molecular weight of the ethylene copolymer produced can be controlled by changing the content of hydrogen in the reaction system or by changing the polymerization temperature, as described in DE 3127133.2.

5 Blends of the ethylene homopolymer of the present invention with a second ethylene homopolymer are also an aspect of the present invention. The second ethylene homopolymer can be one produced by a Ziegler catalyst, a Phillips type Cr-SiO₂ catalyst, or a metallocene-based single site catalyst including the constrained geometry catalysts, used to make the homogeneous narrow composition distribution ethylene interpolymer blend
10 component.. Also included as a the second homopolymer is a homopolymer of the present invention, having different properties from the first, which properties include for example, I_2 , or I_{21}/I_2 , or I_{10}/I_2 , or density, or M_w , or M_w/M_n .

15 If blends of the inventive ethylene polymer with further ethylene interpolymers or homopolymers as described herein, are required, each component can be made separately in different reactors, and subsequently blended together.

The blend compositions may also be produced via a continuous (as opposed to a batch or semi-batch operation) controlled polymerization
20 process using at least one reactor. Preferably, though, the higher density ethylene interpolymer and the additional ethylene interpolymers of the blend compositions are made in a multiple reactor scheme, operated either in parallel or in series, such as those disclosed in USP 3,914,342 (Mitchell) and WO 94/00500. For example, at least two reactors operated
25 in series, that is, one after the other, may be used. Alternatively, the reactors may be operated in parallel, that is, conducting the polymerization steps A and B in separate reactors and subsequently combining melt streams to yield a composite product blend. In the multiple reactor scheme, at least one of the reactors makes the higher
30 density ethylene interpolymer using the supported metallocene catalyst described herein, under gas phase or slurry process conditions, and at least one of the reactors makes the additional components of the blend using the required single or multiple catalysts (or optionally using no additional catalyst fed) at polymerization temperatures, pressures and
35 feed concentrations required to produce the polymer with the desired properties. The reactors may be any of the type commonly used for

ethylene polymerization, including but not restricted to autoclave or loop-type reactors.

Thus in one embodiment, the ethylene polymer, using the supported constrained geometry catalyst described herein, is made under slurry process conditions in a first loop reactor in Step A and the contents of the first reactor passed to a second reactor in which the feed concentrations and the temperature are adjusted, to form under slurry process conditions in Step B either a second ethylene homopolymer or, if comonomer is added, to form, the polyolefin component of the polymer blend having a molecular weight maximum occurring in the fraction having the highest comonomer content.

In a further embodiment, the ethylene polymer, using the supported constrained geometry catalyst described herein, is made under slurry process conditions in a first loop reactor in Step A and the contents of the first loop reactor are passed to a second reactor in which the feed concentrations and the temperature are adjusted, and one or more of the Ziegler catalysts described herein added, to form, in Step B, under slurry process conditions, the heterogeneous ethylene interpolymer component of the polymer blend with the desired properties.

In a further embodiment the ethylene polymer, using the supported constrained geometry catalyst described herein, is made under slurry process conditions in a first loop reactor in Step A and the contents of the first loop reactor enter a second reactor in which the feed concentrations and temperatures are adjusted and one of the metallocene catalysts described herein is added to form the homogeneous component of the polymer blend with the desired properties in Step B under solution process conditions.

In a further embodiment, the ethylene polymer, using the supported constrained geometry catalyst described herein, is made under slurry process conditions in a first loop reactor in Step A and the contents of the first loop reactor are passed to a second reactor in which the temperature and feed concentrations are adjusted, and one or more of the Ziegler catalysts described herein added, to form, in Step B, under solution process conditions, the heterogeneous ethylene interpolymer component of the polymer blend with the desired properties.

In a further embodiment the ethylene polymer, using the supported constrained geometry catalyst described herein, is made under slurry process conditions in a first loop reactor in Step A and the contents of the first loop reactor enter a second reactor in which the feed concentrations and temperatures are adjusted and no additional catalyst is added to form the homogeneous component of the polymer blend with the desired properties in Step B under solution or slurry process conditions.

Additives such as antioxidants (for example, hindered phenolics (for example, IrganoxTM 1010), phosphites (for example, IrgafosTM 168)), cling additives (for example, PIB), antiblock additives, pigments, fillers, and the like can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants. Both IrganoxTM and IrgafosTM are made by and trademarks of Ciba Geigy Corporation. IrgafosTM 168 is a phosphite stabilizer and IrganoxTM 1010 is a hindered polyphenol stabilizer (for example, tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenylpropionate)]methane.

The amount of the ethylene homopolymer of the present invention, incorporated into the blended compositions of the present invention is of from 1 to 99, preferably of from 10 to 90, more preferably of from 25 to 75, most preferably of from 35 to 65 percent, by weight based on the combined weights of Components A and B.

The properties of the ethylene homopolymer of the present invention, incorporated into the blended compositions of the present invention are as described previously.

The amount of the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended compositions of the present invention is of from 1 to 99, preferably of from 10 to 90, more preferably of from 25 to 75, most preferably of from 35 to 65 percent, by weight based on the combined weights of components A and B.

The density of the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is generally of from 0.870 to 0.980, preferably of from 0.890 to 0.965, more preferably of from 0.915 to 0.955 g/cm³.

The melt index (I_2) for the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is generally of from 0.0001 to 10000, preferably of from 0.001 to 5000, more preferably of from 0.01 to 3000 g/10 min.

The I_{21}/I_2 ratio of the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is of from 10 to 50, preferably of from 12 to 45, more preferably of from 15 to 40 or the I_{10}/I_2 ratio of the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is of from 5 to 25, preferably of from 5.3 to 25, more preferably of from 5.5 to 20.

The M_w/M_n ratio of the homogeneous narrow composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention (including the substantially linear ethylene/ α -olefin interpolymer) is less than 3.

The amount of the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended compositions of the present invention is of from 1 to 99, preferably of from 10 to 90, more preferably of from 25 to 75, most preferably of from 35 to 65 percent, by weight based on the combined weights of components A and B.

The density of the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is generally of from 0.870 to 0.980, preferably of from 0.890 to 0.965, more preferably of from 0.915 to 0.955 g/cm³.

The melt index (I_2) for the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is generally of from 0.0001 to 10000, preferably of from 0.001 to 5000, more preferably of from 0.01 to 3000 g/10 min.

The I_{21}/I_2 ratio of the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is of from 15 to 80, preferably of from 20 to 70;

more preferably of from 25 to 60 or the I_{10}/I_2 ratio of the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is of from 5 to 40, preferably of from 5.3 to 35, more preferably of from 5.5 to 30.

5 The M_w/M_n ratio of the heterogeneous broad composition distribution ethylene/ α -olefin interpolymer incorporated into the blended composition of the present invention is generally of from 3 to 12 preferably of from 3.5 to 10, more preferably of from 4 to 9.

10 The amount of polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content, incorporated into the blended compositions of the present invention is of from 1 to 99, preferably of from 10 to 90, more preferably of from 25 to 75, most preferably of from 35 to 65 percent, by weight based on the
15 combined weights of Components A and B.

 The density of the polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content incorporated into the blended compositions of the present invention is generally of from 0.870 to 0.980, preferably of from 0.890 to 0.965, more
20 preferably of from 0.915 to 0.955 g/cm³.

 The melt index of the polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content incorporated into the blended compositions of the present invention is generally of from 0.0001 to 10000, preferably of from 0.001
25 to 5000, more preferably of from 0.01 to 3000 g/10 min.

 The I_{21}/I_2 ratio of the polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content, incorporated into the blended compositions of the present invention is of from 15 to 65, preferably of from 18 to 55, more
30 preferably of from 20 to 50 or the I_{10}/I_2 ratio of the polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content, incorporated into the blended compositions of the present invention is of from 5 to 30, preferably of from 5 to 28, more preferably of from 5.5 to 25.

The M_w/M_n ratio of the polyolefin compositions having a molecular weight maximum occurring in the fraction having the highest comonomer content, incorporated into the blended compositions of the present invention is generally of from 2.5 to 10 preferably of from 2.8 to 8, more preferably of from 3 to 7.

The amount of the second homopolymer, incorporated into the blended compositions of the present invention is of from 1 to 99, preferably of from 10 to 90, more preferably of from 25 to 75, most preferably of from 35 to 65 percent, by weight based on the combined weights of Components A and B.

The density of the second homopolymer incorporated into the blended compositions of the present invention is generally of from 0.870 to 0.980, preferably of from 0.890 to 0.965, more preferably of from 0.915 to 0.955 g/cm³.

The melt index of the second homopolymer incorporated into the blended compositions of the present invention is generally of from 0.0001 to 10000, preferably of from 0.001 to 5000, more preferably of from 0.01 to 3000 g/10 min.

The I_{21}/I_2 ratio of the second homopolymer, incorporated into the blended compositions of the present invention is of from 18 to 70, preferably of from 20 to 60, more preferably of from 10 to 50 or the I_{10}/I_2 ratio of the second homopolymer, incorporated into the blended compositions of the present invention is of from 5 to 40, preferably of from 5.3 to 35, more preferably of from 5.5 to 30.

The M_w/M_n ratio of the second homopolymer, incorporated into the blended compositions of the present invention is generally of from 2.5 to 12, preferably of from 2.8 to 10, more preferably of from 3 to 9.

The density of the final blend compositions of the present invention is generally of from 0.870 to 0.980, preferably of from 0.915 to 0.975, more preferably of from 0.935 to 0.970 g/cm³.

The melt index of the final blend compositions of the present invention is generally of from 0.0001 to 10000 preferably of from 0.001 to 5000, more preferably of from 0.01 to 3000 g/10 min

The I_{21}/I_2 ratio of the final blend compositions of the present invention is of from 20 to 200, preferably of from 30 to 180, more preferably of from 40 to 150 or the I_{10}/I_2 ratio of the final blend compositions of the present invention is of from 5 to 100, preferably of
5 from 5 to 90, more preferably of from 5 to 80.

The M_w/M_n ratio of the final blend compositions of the present invention is generally of from 2.5 to 50, preferably of from 3 to 45, more preferably of from 5 to 40.

Possible applications for the novel resin blends taught by the
10 present invention include pipe, especially pipe used in high temperature applications, geomembranes, wire and cable jacketing, thermoformed articles, stackable plastic pallets, blow molded bottles and containers, rotomolded articles, films, including thick film applications such as environmental pond liners, and vinyl benzocyclobutene cross linking.

15 The present invention is now illustrated by, but is by no means limited to, the following examples.

EXAMPLES

Example 1.

20 Catalyst Preparation.

The supported cocatalyst is a silica/methylalumoxane support having the properties of and prepared substantially as described in WO 96/16092 (prepared by Witco GmbH, lot No. TA 02794/HL/30) containing between 23 and 25 weight percent of aluminum. A 100 g sample of the support is slurried
25 for four hours in 800 ml of hydrocarbon solvent to which is added a hydrocarbon (for example, Isopar™ E supplied by Exxon) solution of the constrained geometry catalyst {(tert-butylamido)dimethyl (tetramethyl- η^5 -cyclopentadienyl)silane}dimethyl-titanium(IV) sufficient to obtain a final catalyst loading of 40 micromole of titanium for one gram of support. The
30 catalyst is transferred to the catalyst feed vessel of the plant. In this vessel, the supported catalyst is further diluted with isobutane to obtain a concentration of 0.5 micromole titanium per ml.

Descriptions of other suitable supported catalyst systems can also be found in US application number 08/857,816 and US application number 08/857,817, as well as in Japanese Application Serial No. 148392/96 and WO 97/43323.

5 Polymerization

The polymerization is performed in a continuous slurry process using a loop reactor. Suitable loop reactors and loop reactor configurations are described in WO 97/36942 and in US Patent No. 5,705,578. US Patent Number 5,705,578 describes suitable slurry loop
10 polymerization conditions to use in conjunction with a supported solid constrained geometry catalyst system described herein. But, although the polymerization description in US Patent Number 5,705,578 is believed to be suitable for the practice of the present invention, the polymerization conditions must operated and adjusted to provide the inventive ethylene
15 polymer disclosed herein. In particular, the slurry loop polymerization reaction is conducted at ethylene conversion rates of greater than 92 percent per pass at polymerization temperatures greater than 84°C using a diluent capable of operating at such conditions while maintaining the polymer produced in a solid state.

What is claimed is:

1. An ethylene homopolymer having long chain branching made by a slurry polymerization process, the homopolymer being characterized as having:

- 5 a) a M_w/M_n ratio greater than 2.5 which satisfies the following inequality:

$$M_w/M_n \geq 22.8 - 3.3 \log M_w$$

- 10 b) a melt index (I_2) of from 0.0001 to 10000 g/10 min., and

- c) a density satisfying the following inequality:
density (g/cm³) > 0.9611 + 0.0058 log (I_2) - 0.00128 log²

2. The ethylene homopolymer of Claim 1, wherein

- 15 a) the density is from 0.915 to 0.985 g/cm³,
b) the I_{10}/I_2 ratio is from 5 to 30 or the I_{21}/I_2 ratio is of from 15 to 65; and
c) the M_w/M_n ratio satisfies the following inequality;

$$M_w/M_n \geq 33.1 - 4.78 \log M_w$$

20

3. The ethylene homopolymer of Claim 1, wherein

- a) the density is from 0.935 to 0.983 g/cm³,
b) the M_w/M_n ratio is from 2.5 to 10,
c) the melt index (I_2) is from 0.001 to 5000 g/10 min.
25 d) the I_{10}/I_2 ratio is from 5 to 28 or the I_{21}/I_2 ratio is of from 18 to 55; and
e) the M_w/M_n ratio satisfies the following inequality;

$$M_w/M_n \geq 45.6 - 6.6 \log M_w$$

4. The ethylene homopolymer of Claim 1, wherein the M_w/M_n ratio satisfies the following inequality:

$$3.1 - 0.15 \log M_w - 2.5 \geq M_w/M_n \geq 22.8 - 3.3 \log M_w.$$

5

5. The ethylene homopolymer of Claim 1 wherein

- a) the density is from 0.945 to 0.980 g/cm³,
- b) the melt index (I_2) is from 0.01 to 3000 g/10 minutes,
- c) the I_{10}/I_2 ratio is from 5.5 to 25 or the I_{21}/I_2 ratio is of
from 20 to 50,
- d) the M_w/M_n ratio is from 3 to 6; and
- e) wherein said homopolymer contains less than 1 ppm catalyst chloride residues and less than 1 ppm catalyst chromium residues.

10

15

6. An ethylene homopolymer, having long chain branching and made by a slurry polymerization process, the homopolymer being characterized as having:

- a) an M_w/M_n ratio greater than 2.5,
- b) a melt index (I_2) of from 0.0001 to 10000 g/10 min,
- c) a density which satisfies the following inequality;
density (g/cm³) > 0.9611 + 0.0058 log (I_2) - 0.00128 log² (I_2);

and

- e) wherein the homopolymer contains less than 1 ppm catalyst chloride residues and less than 1 ppm catalyst chromium residues.

25

7. An ethylene homopolymer having long chain branches made by a process, the process comprising polymerizing ethylene under slurry process conditions with a catalyst comprising:

(I) a supported catalyst component resulting from admixing:

(A) a support material;

(B) an organometal compound which is a member of Groups 2-13 of the Periodic Table of the Elements, germanium, tin, or lead;

(C) an activator compound containing a cation which is capable of reacting with a transition metal compound to form a catalytically active transition metal complex, and a compatible anion having up to 100 nonhydrogen atoms and containing at least one substituent comprising an active hydrogen moiety; and

(D) a transition metal compound; or

(II) a supported catalyst component resulting from admixing

(A) a support material and an alumoxane which component contains 15 to 40 weight percent of aluminum, based on the total weight of the support material and alumoxane, which is obtained by;

(a) heating said support material and alumoxane under an inert atmosphere for a period and at a temperature sufficient to fix alumoxane to the support material, to provide a supported catalyst component wherein not more than 10 percent aluminum present in the supported catalyst component is extractable in a one-hour extraction with toluene at 90°C using 10 ml toluene per gram of supported catalyst component; and

(b) optionally, subjecting the product produced in step (a) to one or more wash steps to remove alumoxane not fixed to the support material; and

(B) a transition metal compound; or

(III) any combination of (I) and (II).

8. The ethylene homopolymer of Claim 7 wherein the supported catalyst component is obtained in prepolymerized form by subjecting the supported catalyst, in the presence of an olefin, to polymerization conditions.

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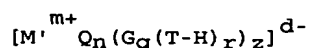
9. The ethylene homopolymer of Claim 7 wherein

- (i) the supported catalyst component has an aluminum atom to transition metal atom mole ratio of from 1:1 to 5,000:1;
- (ii) the supported catalyst component contains of from 0.1 to 1000 micromoles of transition metal compound per gram of support material;
- (iii) the supported catalyst component contains of from 0.1 to 1000 micromoles of transition metal compound per gram of support material;
- (iv) the supported catalyst component contains of from 0.1 to 1,000 micromoles of transition metal compound per gram of support material;
- (v) the organometal compound is an aluminum component comprising an alumoxane, or an aluminum compound of the formula AlR^1_x wherein R^1 independently in each occurrence is hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms, and x is 3, or a combination thereof;
- (vi) component (I) is prepared by any one of:
 - (1) subjecting a support material to a thermal treatment at a temperature of from 100°C to 1,000°C; combining the thermally treated support material with the organometal compound in a suitable diluent or solvent; and subsequently combining the resulting product with the activator compound and finally adding the transition metal compound; or
 - (2) combining the activator compound with the organometal compound to form an adduct; combining the adduct with the support material which contains water or has been subjected to a thermal treatment at a temperature of from 100°C to 1,000°C and finally adding the transition metal compound; or

- (3) combining a water containing support material with the organometal compound; and combining the resulting product with the activator compound; and finally with a transition metal compound;
- 5 (vii) in supported catalyst component (I), the organometal compound is an aluminum component selected from the group consisting of alumoxane, an aluminum compound of the formula AlR^1_x , wherein R^1 independently in each occurrence is hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms, and x is 3, and a combination thereof;
- 10 (viii) in component 1, the cation portion of the activator compound is selected from the group consisting of Brønsted acid cations, carbonium cations, silylium cations, and cationic oxidizing agents, and in the anion portion of the activator compound the substituent comprising an active hydrogen moiety corresponds to the following formula,
- 15
$$G_q(T-H)_r$$
 wherein G is a polyvalent hydrocarbon radical, T is O, S, NR, or PR, wherein R is a hydrocarbyl radical, a trihydrocarbylsilyl radical, a trihydrocarbyl germyl radical or hydrogen, q is 0 or 1, and r is an integer from 1 to 3;
- 20 (ix) in supported catalyst component (II), alumoxane is methylalumoxane;
- 25 (x) in supported catalyst component (II), not more than 9 percent aluminum present in the supported catalyst component is extractable in a one-hour extraction with toluene at 90°C using 10 ml toluene per gram of
- 30 supported catalyst component;
- (xi) in supported catalyst component (II), aluminum is present in an amount of from 20 to 40 weight percent based on the total weight of the support material and methylalumoxane;
- 35 (xii) in supported catalyst component (II), heating step (a) is followed by (b) which is accomplished by slurrying the supported catalyst component in an aromatic

hydrocarbon and heating the slurry under reflux conditions of said aromatic hydrocarbon; and
 (xiii) the support material comprises silica, alumina, or mixed oxides of;
 5 (a) silica; and
 (b) one or more Group 2 or 13 metal oxides, alumina, magnesia, or titania; and
 (xiv) the M_w/M_n ratio is greater than or equal to 3.29.

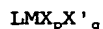
10 10. The ethylene homopolymer of Claim 7 wherein
 (i) in component 1, the anion portion of the activator compound corresponds to the formula:



wherein:

15 M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements;
 Q independently in each occurrence is selected from the group consisting of hydride, dihydrocarbylamido, halide, hydrocarbyloxy, hydrocarbyl, and substituted-
 20 hydrocarbyl radicals, including halo-substituted hydrocarbyl radicals, and hydrocarbyl- and halohydrocarbyl-substituted organo-metalloid radicals, the hydrocarbyl portion having from 1 to 20 carbons with the proviso that in not more than one occurrence is Q
 25 halide;
 G is a polyvalent hydrocarbon radical having r+1 valencies bonded to M' and T;
 T is O, S, NR, or PR, wherein R is a hydrocarbyl radical, a trihydrocarbylsilyl radical, a trihydrocarbyl germyl
 30 radical or hydrogen;
 m is an integer from 1 to 7;
 n is an integer from 0 to 7;
 q is an integer of 0 or 1;
 r is an integer from 1 to 3;
 35 z is an integer from 1 to 8;
 d is an integer from 1 to 7; and
 n+z-m = d; and

(ii) said transition metal compound in either supported catalyst components (I) or (II) corresponds to the formula:



5

wherein:

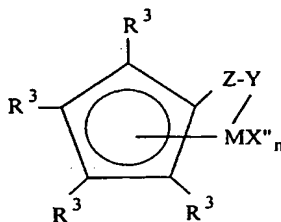
- M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4, bound in an η^5 bonding mode to one or more L groups;
- L independently each occurrence is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group optionally substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, aminohydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, dihydrocarbylphosphino, silyl, aminosilyl, hydrocarbyloxysilyl, and halosilyl groups containing up to 20 non-hydrogen atoms, or further optionally two such L groups may be joined together by a divalent substituent selected from hydrocarbadiyl, halohydrocarbadiyl, hydrocarbyleneoxy, hydrocarbyleneamino, siladiyl, halosiladiyl, and divalent aminosilane, groups containing up to 20 non-hydrogen atoms;
- X independently each occurrence is a monovalent anionic σ -bonded ligand group, a divalent anionic σ -bonded ligand group having both valences bonded to M, or a divalent anionic σ -bonded ligand group having one valency bonded to M and one valency bonded to an L group, wherein X contains up to 60 nonhydrogen atoms;
- X' independently each occurrence is a neutral Lewis base ligating compound, selected from the group comprising phosphines, ethers, amines; olefins; or a conjugated diene having from 4 to 40 carbon atoms; or both;
- p is 0, 1 or 2, and is 1 less than the formal oxidation state of M when X is an monovalent anionic σ -bonded ligand group or a divalent anionic σ -bonded ligand group

having one valency bonded to M and one valency bonded to an L group, or p is 2 less than the formal oxidation state of M when X is a divalent anionic σ -bonded ligand group having both valencies bonded to M; and

q is 0, 1 or 2.

11. The ethylene homopolymer of Claim 10, wherein X' is tetrahydrofuran, pyridine, bipyridine, tetramethylethylenediamine (TMEDA), triethylamine, trimethylphosphine, triethylphosphine, triphenylphosphine, bis(1,2-dimethylphosphino)ethane, or P(OR), wherein R is a C₁-C₃₀ hydrocarbyl.

12. The ethylene homopolymer of Claim 10, wherein the transition metal compound corresponds to the formula:



15

wherein:

M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

R³ in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R³ having up to 20 non-hydrogen atoms, or adjacent R³ groups together form a divalent derivative selected from the group consisting of a hydrocarbadiyl, siladiyl or germadiyl group, thereby forming a fused ring system,

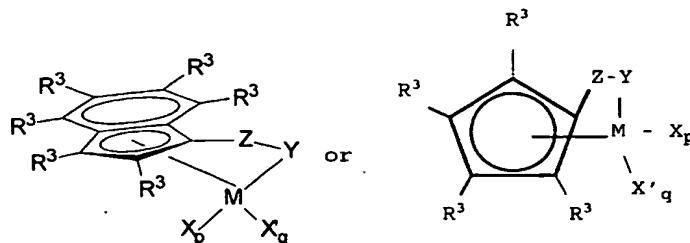
25 each X'' is independently, a halo, hydrocarbyl, hydrocarbyloxy, hydrocarbylamino, or silyl group, said group having up to 20 non-hydrogen atoms, or two X'' groups together form a neutral C₅₋₃₀ conjugated diene or a divalent derivative thereof;

Y is -O-, -S-, -NR*- , -PR*- ;

30 Z is SiR*₂, CR*₂, SiR*,SiR*₂, CR*,CR*₂, CR*=CR*, CR*,SiR*₂, or GeR*₂, wherein R* is a C₁₋₄ alkyl or phenyl, and

n is an integer from 1 to 3.

13. The ethylene homopolymer of Claim 10 wherein the transition metal compound corresponds to the formula:



5 wherein:

R^3 independently each occurrence is hydrogen, hydrocarbyl, halohydrocarbyl, silyl, germyl and mixtures thereof, containing up to 20 nonhydrogen atoms;

M is titanium, zirconium or hafnium;

10 Z , Y , X and X' are as previously defined;

p is 0, 1 or 2; and

q is zero or one;

with the proviso that:

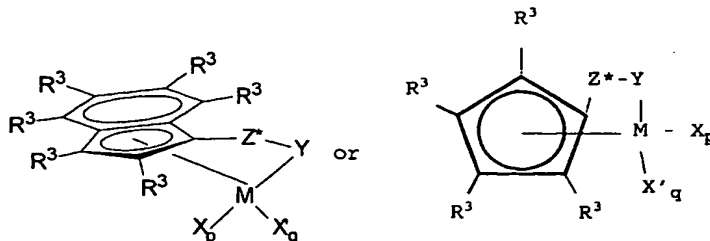
when p is 2, q is zero, M is in the +4 formal oxidation state, and X is an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido,

15 di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy- and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 20 nonhydrogen atoms,

when p is 1, q is zero, M is in the +3 formal oxidation state, and X is a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N -dimethylaminomethyl)phenyl, and 2-(N,N -dimethyl)-aminobenzyl, or M is in the +4 formal oxidation state, and X is a divalent derivative of a conjugated diene, M and X together forming a metallocyclopentene group, and

25 when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M .

14. The ethylene homopolymer of Claim 10 wherein the transition metal compound corresponds to the formula:



wherein:

- 5 R³ independently each occurrence is hydrogen or C₁₋₆ alkyl;
 M is titanium;
 Y is -O-, -S-, -NR*- , -PR*-;
 Z* is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, or GeR*₂;
 R* each occurrence is independently hydrogen, or a hydrocarbyl,
 10 hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, or combinations thereof, said R* having up to 20 non-hydrogen atoms, and optionally, two R* groups from Z (when R* is not hydrogen), or an R* group from Z and an R* group from Y form a ring system;
 p is 0, 1 or 2;
 15 q is zero or one; and
 with the proviso that:
 when p is 2, q is zero, M is in the +4 formal oxidation state, and X is independently each occurrence methyl or benzyl;
 when p is 1, q is zero, M is in the +3 formal oxidation state, and X is
 20 2-(N,N-dimethyl)aminobenzyl; or M is in the +4 formal oxidation state and X is 2-butene-1,4-diyl, and
 when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene.

- 25 15. A polymer blend composition comprising
 (A) an ethylene homopolymer in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B), the homopolymer being made by a slurry polymerization process and having long chain branches, a M_w/M_n ratio (as measured by GPC)
 30 greater than 2.5, and a density which satisfies the following inequality:
 density (g/cm³) > 0.9611 + 0.0058 log (I₂) - 0.00128 log² (I₂); and
 wherein the homopolymer contains less than 1 ppm catalyst chloride residues and less than 1 ppm catalyst chromium residues.
 35 (B) an ethylene/α-olefin interpolymer or an ethylene homopolymer other than one having the identical properties of Component (A), wherein the interpolymer or homopolymer are present

in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B).

16. A polymer blend composition comprising:

(A) an ethylene homopolymer in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B), the homopolymer being made by a slurry polymerization process and having long chain branches, a M_w/M_n ratio (as measured by GPC) greater than 2.5, a density which satisfies the following inequality;

$$\text{density (g/cm}^3\text{)} > 0.9611 + 0.0058 \log (I_2) - 0.00128 \log^2 (I_2);$$

and an M_w/M_n which satisfies the following inequality:

$$M_w/M_n \geq 22.8 - 3.3 \log M_w; \text{ and}$$

(B) an ethylene/ α -olefin interpolymer or an ethylene homopolymer other than one of Component (A) having the identical properties, wherein said interpolymer or homopolymer are present in an amount of from 1 to 99 percent by weight based on the combined weight of Components (A) and (B).

17. The polymer blend composition of Claim 16, wherein Component (B) comprises:

- (1) a homogeneous narrow composition distribution ethylene/ α -olefin interpolymer.; or
- (2) a heterogeneous broad composition distribution ethylene/ α -olefin interpolymer; or
- (3) an ethylene interpolymer made by a slurry polymerization process and having a molecular weight maximum occurring in the fraction having the highest comonomer content prepared with the same catalyst as used to make said homopolymer of Claim 1 to 6; or
- (4) an ethylene homopolymer having a different I_2 , or density or M_w or M_w/M_n than Component (A); or
- (5) a combination of any two or more of (B) (1), (B) (2), (B) (3), or (B) (4).

18. The polymer blend composition of Claim 17, having

- a) a density of from 0.87 to 0.98 g/cm³,
- b) a melt index (I_2) of from 0.0001 to 10000 g/10 minutes,
- c) an I_{21}/I_2 of from 20 to 200, or an I_{10}/I_2 of from 5 to 100, and
- d) an M_w/M_n ratio of from 2.5 to 50; and wherein

(I) Component (A) is present in an amount of from 10 to 90 percent by weight based on the combined weight of Components (A) and (B); and has

- a) a density of from 0.915 to 0.985 g/cm³,
- 5 b) a melt index (I_2) of from 0.0001 to 10,000 g/10 min.,
- c) an I_{21}/I_2 of from 15 to 65, or an I_{10}/I_2 of from 5 to 30, and
- d) a M_w/M_n ratio of from 2.5 to 10; and
- e) a M_w/M_n ratio which satisfies the following inequality;
- 10 $M_w/M_n \geq 33.1 - 4.78 \log M_n$; and

(II) Component B is present in an amount of from 10 to 90 percent by weight based on the combined weight of Components (A) and (B), and has:

- a) a density of from 0.87 to 0.98 g/cm³,
- 15 b) a melt index (I_2) of from 0.0001 to 10000 g/10 min. and wherein
 - i) Component B(1) has an I_{21}/I_2 of from 10 to 50 or an I_{10}/I_2 of from 5 to 25; and
 - ii) Component B(2) has:
 - 20 a) an I_{21}/I_2 of from 15 to 80 or an I_{10}/I_2 of from 5 to 40, and;
 - b) a M_w/M_n of from 3 to 12; and
 - iii) Component B(3) has
 - 25 a) an I_{21}/I_2 of from 15 to 65, or an I_{10}/I_2 of from 5 to 30, and
 - b) an M_w/M_n of from 2.5 to 10; and
 - c) a slope of cross-fractionation in the range from -1 to -0.005, and
 - iv) Component B(4) has;
 - 30 a) an I_{21}/I_2 of from 18 to 70 or an I_{10}/I_2 of from 5 to 40; and

b) a M_w/M_n of from 2.5 to 12.

19. The polymer blend composition of Claim 18 having:

- a) a density of from 0.915 to 0.975 g/cm³; and
 b) a melt index (I_2) of from 0.001 to 5000 g/10 minutes;

and

- c) an I_{21}/I_2 of from 30 to 180, or an I_{10}/I_2 of from 5 to 90,
 and

- d) a M_w/M_n ratio of from 3 to 45; and

wherein

(I) Component (A) is present in an amount of from 25 to 75 percent by weight based on the combined weight of Components (A) and (B), and has:

- a) a density of from 0.935 to 0.983 g/cm³; and
 b) a melt index (I_2) of from 0.001 to 5,000 g/10 min.; and
 c) an I_{21}/I_2 of from 18 to 55, or an I_{10}/I_2 of from 5 to 28;
 and
 d) a M_w/M_n ratio of from 2.8 to 8; and
 e) a M_w/M_n ratio which satisfies the following inequality;

$$M_w/M_n \geq 45.6 - 6.6 \log M_w; \text{ and}$$

(II) Component B is present in an amount of from 25 to 75 percent by weight based on the combined weight of Components (A) and (B), and has;

- a) a density of from 0.89 to 0.965 g/cm³; and
 b) a melt index (I_2) of from 0.001 to 5000 g/10 min.; and
 wherein

- i) Component B(1) has an I_{21}/I_2 of from 12 to 45, or an I_{10}/I_2 of from 5.3 to 25; and

- ii) Component B(2) has:

- a) an I_{21}/I_2 of from 20 to 70, or an I_{10}/I_2 of from 5.3 to 35; and

- b) a M_w/M_n of from 3.5 to 10; and

- iii) Component B(3) has:

- a) an I_{21}/I_2 of from 18 to 55, or an I_{10}/I_2 of from 5 to 28, and

- b) a M_w/M_n of from 32.8 to 8; and
- c) a slope of cross-fraction in the range from -0.5 to -0.007, and
- d) a sum of extractives at reduced temperatures of 5 percent by weight or less, based on the total amount of interpolymer fractions extracted at temperatures in the overall range of extraction temperatures in cross-fractionation chromatography (CFC), excluding purge; and
- e) within a range in molecular weight for Component (B)(3), which is defined by the formula):
- $$\log (M_t) - \log (M_c) \leq 0.5,$$
- a slope of molecular weight to comonomer distribution, as determined using gel permeation chromatography/Fourier transformation infrared spectroscopy (GPC/FT-IR), in the range of 0.0005 to 0.05;
- iv) Component B(4) has:
- a) an I_{21}/I_2 of from 20 to 60 or an I_{10}/I_2 of from 5.3 to 35; and
- b) a M_w/M_n of from 2.8 to 10.
20. The polymer blend composition according to Claim 19 having:
- a) a density of from 0.935 to 0.970 g/cm³;
- b) a melt index (I_2) of from 0.01 to 3000 g/10 min.; and
- c) an I_{21}/I_2 of from 40 to 150, or an I_{10}/I_2 of from 5 to 80; and
- d) a M_w/M_n ratio of from 5 to 40; and wherein
- (I) Component A is present in an amount of from 35 to 65 percent by weight based on the combined weight of Components (A) and (B), and has;
- a) a density of from 0.945 to 0.980 g/cm³; and
- b) a melt index (I_2) of from 0.01 to 3,000 g/10 min.; and

c) an I_{21}/I_2 of from 20 to 50, or an I_{10}/I_2 of from 5.5 to 25; and

d) an M_w/M_n ratio of from 3 to 6; and

e) an M_w/M_n ratio which satisfies the following inequality;

$$3.1 - 0.15 \log M_w - 2.5 \geq M_w/M_n \geq 22.8 - 3.3 \log M_w; \text{ and}$$

(II) Component B is present in an amount of from 35 to 65 percent by weight based on the combined weight of Components (A) and (B), and has;

a) a density of from 0.915 to 0.955 g/cm³; and

b) a melt index (I_2) of from 0.01 to 3000 g/10 min; and wherein;

i) Component B(1) has;

a) an I_{21}/I_2 of from 15 to 40, or an I_{10}/I_2 of from 5.5 to 20; and

b) an M_w/M_n less than 3; and

ii) Component B(2) has;

a) an I_{21}/I_2 of from 25 to 60, or an I_{10}/I_2 of from 5.5 to 30; and

b) an M_w/M_n of from 4 to 9; and

iii) Component B(3) has;

a) an I_{21}/I_2 of from 20 to 50, or an I_{10}/I_2 of from 5.5 to 25; and

b) an M_w/M_n of from 3 to 7 and wherein;

c), with respect to property (iii)(c) for Component (B) (3), said approximate straight line obtained from said molecular weight distribution profile obtained by CFC of said polymer fraction has a gradient with the range defined by the following formula (V):

$$-0.1 \leq \{ \log M_p(T^1) - \log M_p(T^2) \} / (T^1 - T^2) \leq -0.01 \quad (V)$$

wherein T^1 , T^2 , $Mp(T^1)$ and $Mp(T^2)$ are as defined in Claim 18; and wherein

5 d) with respect to property (iii)(d) for Component (B)(3), said sum of respective amounts of copolymer fractions extracted at temperatures which are at least 10°C lower than said first temperature is 3.5 percent by weight or less, based on the total amount, excluding purge, of
10 copolymer fractions extracted at temperatures in the overall range of extraction temperatures in CFC; and

e) wherein, with respect to property (iii)(e) for Component (B)(3), said approximate straight line obtained from said comonomer content distribution profile obtained by GPC/FT-IR of said ethylene comonomer has a gradient within the range defined by the following formula (VI):

$$0.001 \leq \{C(Mc^1) - C(Mc^2)\} / (\log Mc^1 - \log Mc^2) \leq 0.02 \quad (VI)$$

20 wherein Mc^1 , Mc^2 , $C(Mc^1)$ and $C(Mc^2)$ are as defined in Claim 19; and

iv) Component B(4) has;

a) an I_{21}/I_2 of from 10 to 50 or an I_{10}/I_2 of from 5.5 to 30; and

b) an M_w/M_n of from 3 to 9.

25

21. The polymer blend composition according to Claim 18, wherein, with respect to property (iii)(c) for Component (B)(3), said approximate straight line obtained from said molecular weight distribution profile obtained by CFC of said polymer fraction has a gradient with the range
30 defined by the following formula (VII):

$$-0.08 \leq \{\log Mp(T^1) - \log Mp(T^2)\} / (T^1 - T^2) \leq -0.02 \quad (VII)$$

WHEREIN T^1 , T^2 , $MP(T^1)$ AND $MP(T^2)$ ARE AS DEFINED IN CLAIM 18.

35

22. The polymer blend composition of Claim 17, wherein Component (B1) contains long chain branches.

23. The polymer blend composition of Claim 17, wherein Component (B1) contains long chain branches in the range of 0.01 to 3 per 1000 carbon atoms.

24. The polymer blend composition of Claim 17, wherein Component (B1) contains long chain branches in the range of 0.1 to 3 per 1000 carbon atoms, and has a molecular weight distribution, M_w/M_n , defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63.$$

25. The polymer blend composition of Claim 17 wherein Component B is Component (B) (3) which comprises a copolymer of ethylene with at least one comonomer selected from the group consisting of a compound represented by the formula $H_2C=CHR$ wherein R is a C_1 - C_{20} linear, branched or cyclic alkyl group or a C_6 - C_{20} aryl group, and a C_4 - C_{20} linear, branched or cyclic diene, prepared by a process, which process comprises copolymerizing said ethylene with said comonomer by slurry polymerization in the presence of a solid catalyst system comprising (I) a supported catalyst component resulting from admixing:

(A) a support material;

(B) an organometal compound which is a member of Groups 2-13 of the Periodic Table of the Elements, germanium, tin, or lead;

(C) an activator compound containing a cation which is capable of reacting with a transition metal compound to form a catalytically active transition metal complex, and a compatible anion having up to 100 nonhydrogen atoms and containing at least one substituent comprising an active hydrogen moiety; and

(D) a transition metal compound; or

(II) a supported catalyst component resulting from admixing

(A) a support material and an alumoxane which component contains 15 to 40 weight percent of aluminum, based on the total weight of the support material and alumoxane, which is obtained by;

(a) heating said support material and alumoxane under an inert atmosphere for a period and at a temperature sufficient to fix alumoxane to the support material, to provide a supported catalyst component wherein not more than 10 percent aluminum present in the supported catalyst

component is extractable in a one-hour extraction with toluene at 90°C using 10 ml toluene per gram of supported catalyst component; and

5 (b) optionally, subjecting the product produced in step (a) to one or more wash steps to remove alumoxane not fixed to the support material; and

(B) a transition metal compound; or
(III) any combination of I and II.

10 26. A process for forming a polymer blend composition, which process comprises the steps of:

(I) preparing the ethylene homopolymer (A) of Claim 7;
(II) contacting under polymerization conditions a feedstream comprising ethylene, optionally at least one α -olefin comonomer, and
15 an ethylene polymerization catalyst, to form (B) an ethylene homopolymer or ethylene/ α -olefin interpolymer; and
(III) combining the ethylene homopolymer (A) with the ethylene homopolymer or ethylene/ α -olefin interpolymer (B) to form
(C) the polymer blend composition.

20 27. The process of Claim 26 wherein steps (I) and (II) are performed in different reactors.

25 28. The process of Claim 27 wherein the reactors are operated in series and step (I) is performed in the first reactor(s) and step (II) is performed in the second reactor(s); or, optionally, step (II) is performed in the first reactor(s) and step (I) is performed in the second reactor(s).

30 29. The process of Claim 26 wherein;
(a) step (II) is performed under slurry phase polymerization conditions, or solution phase polymerization conditions, or gas phase polymerization conditions; and
(b) the ethylene polymerization catalyst used in step (II) is
35 a Ziegler catalyst, or an unsupported single site catalyst, or a supported single site catalyst, or a mixture of any two or more of said ethylene polymerization catalysts.

40 30. The process of Claim 29 wherein;
(c) the supported single site catalyst comprises a supported constrained geometry catalyst.

31. The process of Claim 26 wherein the ethylene polymerization catalyst of step (II) is the supported catalyst component described in claim 5.

5 32. The process of Claim 26 wherein the ethylene polymerization catalyst of step (II) is a Ziegler ethylene polymerization catalyst comprising;

- (a) a solid support component is a magnesium halide or silica, and
- (b) a transition metal component represented by the formulas:
10 $\text{TrX}'_4\text{-q(OR}^1\text{)}_q$, $\text{TrX}'_4\text{-qR}^2\text{q}$, VOX'_3 and $\text{VO (OR}^1\text{)}_3$, wherein:
Tr is a Group IVB, VB, or VIB metal,
q is 0 or a number equal to or less than 4,
X' is a halogen, and
R¹ is an alkyl group, aryl group or cycloalkyl group having
15 from 1 to 20 carbon atoms, and
R² is an alkyl group, aryl group, aralkyl group, or substituted aralkyl group.

20 33. The process of Claim 27 wherein the reactors are operated in parallel.

25 34. The process of Claim 26 wherein the α -olefin interpolymer of step (II) has a lower density and a higher molecular weight than the homopolymer produced in step (I).

35 35. The process of Claim 26 wherein the comonomer of step (II) is a C₃-C₂₀ α -olefin.

30 36. The process of Claim 26 wherein the comonomer of step (II) is propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, or 1-octene.

35 37. The polymer blend composition prepared by the process of Claim 26.

38. The sintering powder made from the ethylene homopolymer of Claim 1.

40 39. A fabricated article made from the polymer blend composition of Claim 16.

40. A fabricated article of Claim 39 which is in the form of a film, fiber, coating or sheet, or the result of a thermoforming, blow molding, injection molding and rotational molding process.

- 5 41. A fabricated article of Claim 39 comprising pipes, tubing, cable or wire jackets, pipe coatings, geomembranes, thermoformed articles, stackable plastic pallets, blow molded bottles or containers, or environmental pond liners.

FIG. 1

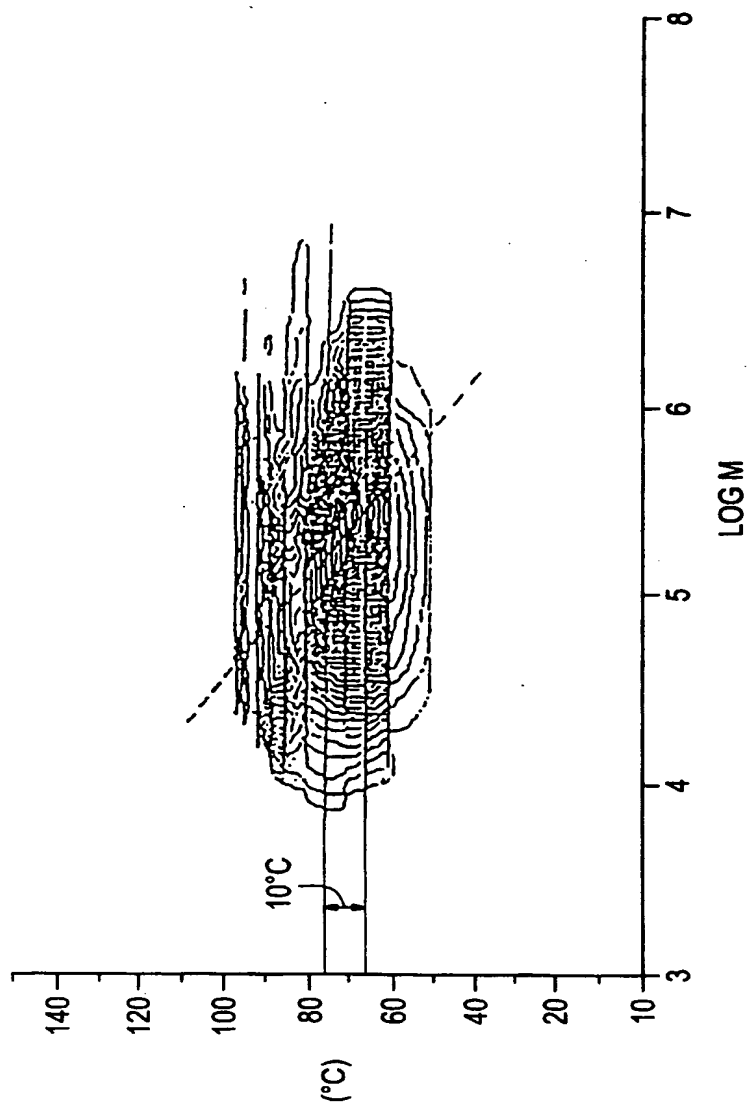


FIG. 2

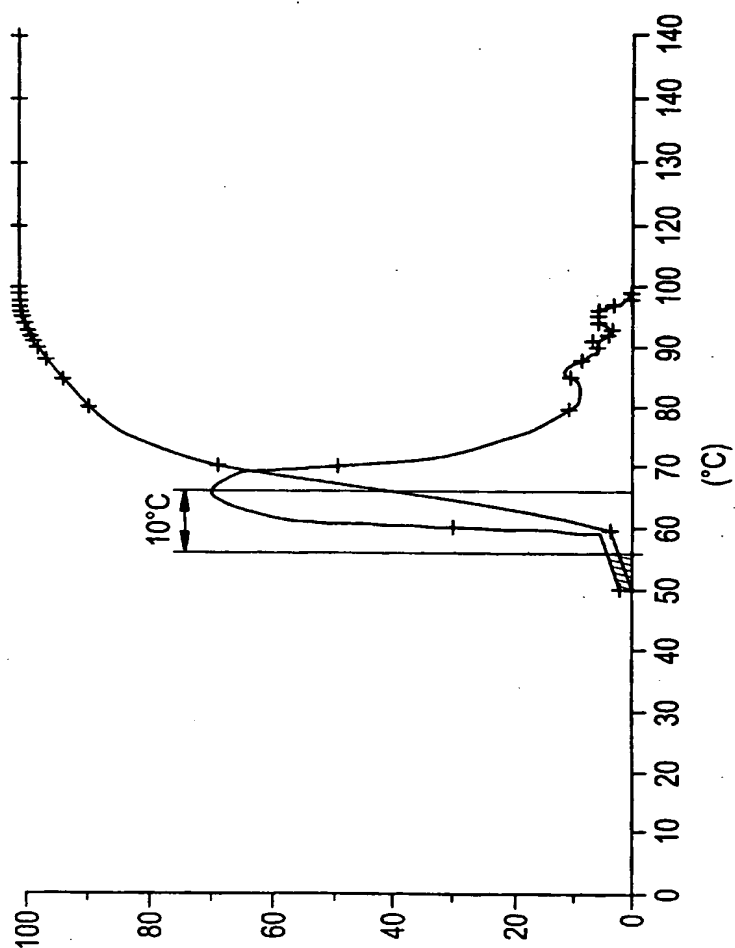
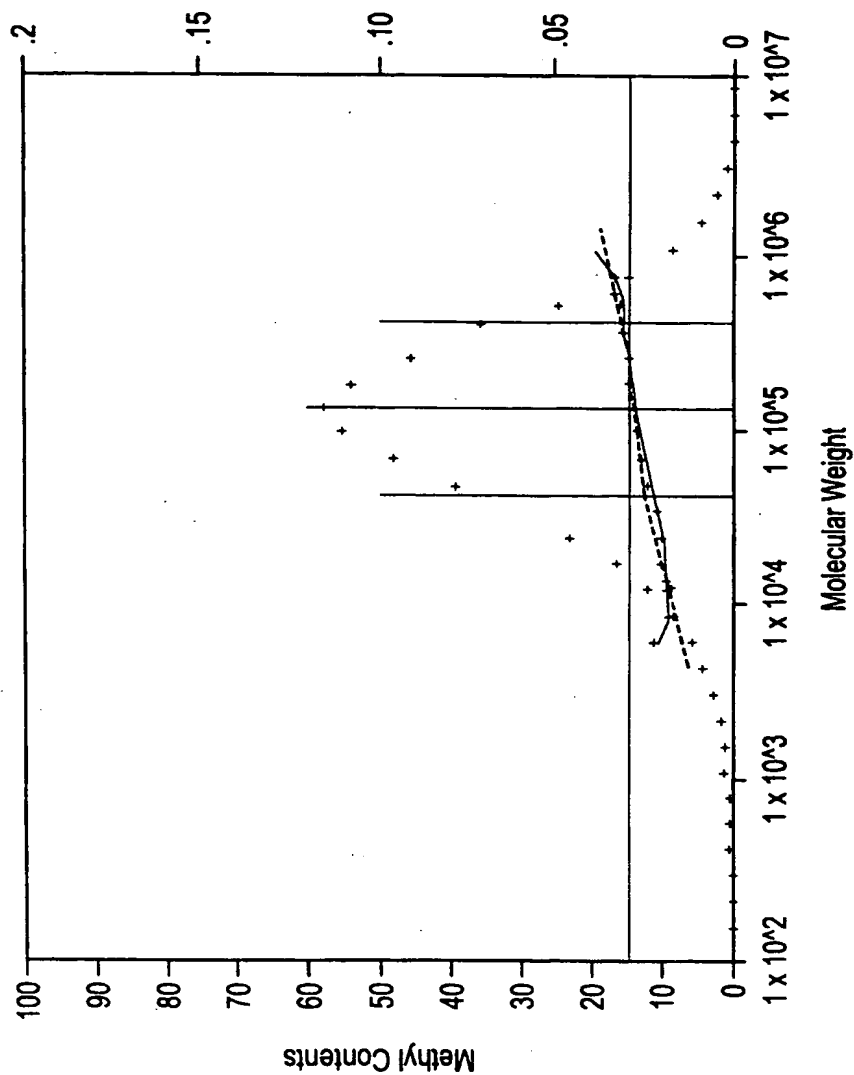


FIG. 3



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International Application No
PCT/US 99/20243

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08F110/02 C08F297/08 C08F2/14 C08L23/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 20 December 1999		Date of mailing of the international search report 12/01/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Kaumann, E

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